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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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AUGUST, 1910

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PHYSICAL REVIEW.

TEMPERATURE- AND POTENTIAL-PRESSURE RELATIONS IN THE MERCURY ARC.

By C. T. Knipp.

IT has been shown quite conclusively that the average temperature of the mercury arc increases from relatively low to very high values depending upon the voltage impressed and the form of the lamp used. Among those who have made temperature measurements are Hewitt, Wills, Küch and Retschinsky. The method employed was to introduce a thermoelement into the arc. Hewitt[1] and Wills[2] each fused their junctions into the walls of the tube and thus made temperature observations at a number of fixed points along its axis.

In 1904 Stark,[3] in commenting upon the probable temperature of the arc at the cathode, pointed out that, from a consideration of the energy consumption and the fact that since the area of the active cathode mercury surface is small in comparison to the whole mercury surface, we should expect the temperature to be fairly high. He concluded after giving additional evidence that the temperature must be at a yellow or white heat. This need not necessarily be an indication of the temperature at points distant from the cathode.

Recently Küch and Retschinsky[4] made a series of observations extending over a wide range of temperature. They worked with a

[1]Hewitt, P. C., Elect. World, Vol. 42, Dec. 19, 1903.
[2]Wills, A. P., Phys. Rev., Vol. XIX., Aug., 1904.
[3]Stark, J., Phys. Zeitschr., Vol. 5, Nov. 15, 1904.
[4]Küch and Retschinsky, Ann. d. Physik., Vol. 22, March 5, 1907.

special quartz lamp using a Pt and Pt-Rh thermo-junction encased in a quartz capillary tube that was fused transversely through the lamp. Three such junctions were mounted in the tube midway between the electrodes. One was placed on the axis and the other on either side near the walls. They found that the curves showing the rise of temperature were different for the three junctions. The temperature recorded by the central one was the higher, and its curve was a straight line showing that the rise of temperature was directly proportional to the potential difference. Temperatures were observed up to about 1700° C.

In a paper read before the American Physical Society[1] the author presented data on the average temperature at three different points

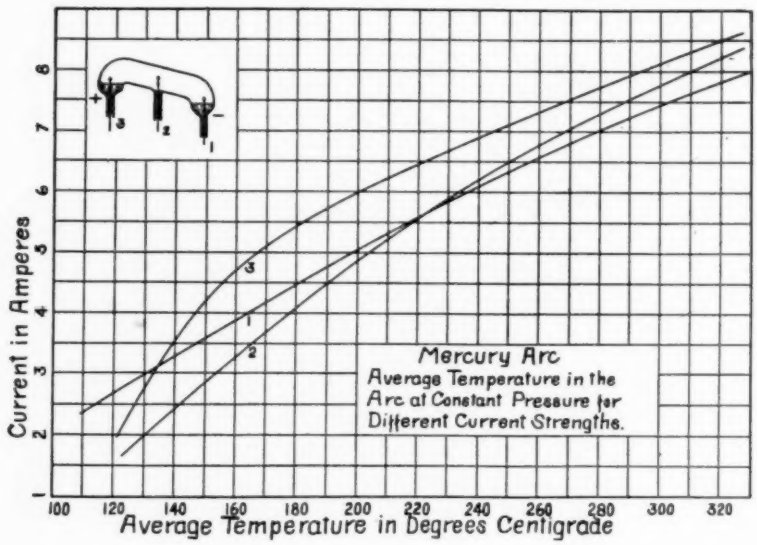

Fig. 1.

in the mercury arc at constant pressure and for different current strengths. The form of the tube employed and the positions of the thermo-junctions are shown in Fig. 1, as also are the curves plotted from the data obtained. In this work no attempt was made to correct the temperatures for the conduction of heat away from the junctions. The curves may have been nearly correct relatively,

[1]Abstract in PHYS. REV., Vol. XXIV., May, 1907.

yet the error due to this was certainly very great, since the junctions projected only about 15 mm. above the surfaces of the comparatively cool mercury electrodes.

In the investigations cited above the temperatures were measured at a comparatively few points and these were for the most part fixed. In the present investigation an effort was made to determine the temperature gradients from electrode to electrode under various conditions of pressure and current and form of tube. During the early stages of the work a paper was read before the November meeting of the American Physical Society, 1908. Potential readings are also included.

Apparatus.

The general arrangement of the apparatus is shown in Fig. 2. The tube *MN*, in which the arc was maintained, had an inside

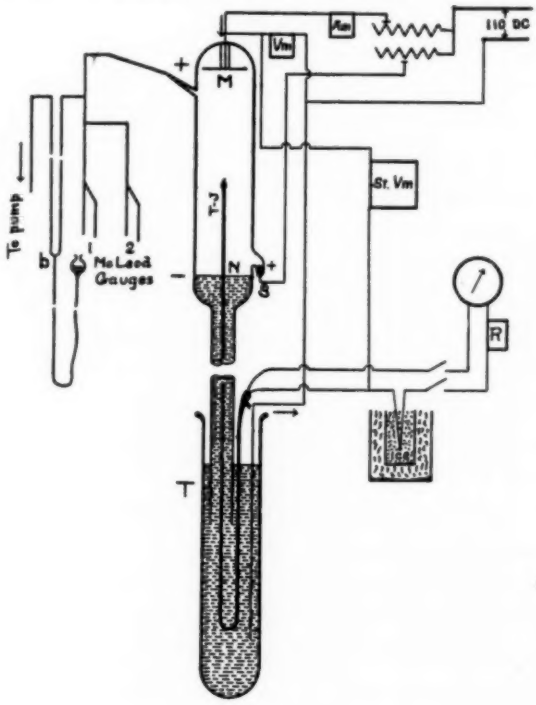

Fig. 2.

diameter of 34 mm. The wide portion of the tube was approximately 235 mm. long. To the lower end was fused a barometric

leg which dipped into a large and thick-walled test-tube T. The tube MN was connected to a power Geryk pump through the barometric valve b. Two McLeod gauges, one large and the other small, were connected as shown. The anode was of platinum and designed for currents up to nine amperes. The cathode was the mercury surface forming the top of the barometric column TN. The usual side branch for starting the arc is shown at S.

The exploring thermo-junction was introduced into the arc by being mounted in a long heavy-walled capillary glass tube having a small and rather thin-walled bulb at its upper end. In making the Cu-Pt couple the platinum wire was allowed to project through the globule of copper about 3 mm. This platinum tip was fused into the glass bulb, from within out, and the projecting portion bent at right angles as shown in the figure. Thus it will be seen the junction was protected from the mercury vapor by the glass envelope, and also that it was in contact with air at normal pressure. The latter served to facilitate the conduction of heat from the walls of the glass envelope to the junction. The platinum wire projecting into the arc served also the same purpose, and in addition it was used as an exploring terminal for reading potentials. The various connections for reading pressures, temperatures, potentials and currents are shown diagrammatically in Fig. 2.

The temperature readings were taken by a copper-platinum thermo-junction calibrated by means of a standard mercurial thermometer and also by means of the sulphur and zinc points. The exploring terminal, T–J in the figure, could be moved readily from anode to cathode, and also from side to side of the tube MN. Nearly all of the readings, however, were taken along the axis. To keep the junction central it was only necessary to sight it from two positions at right angles to each other.

Potential differences from the anode to the exploring potential terminal were read off on a semi-portable laboratory standard Weston voltmeter, while total potential differences were read by an ordinary Weston instrument. In the data that follow unless otherwise stated the arc was kept at a constant length of 224 mm. Its length was adjusted readily by raising or lowering the large test-tube T.

In the form of tube employed there was no condensing chamber, since for the low values of current used it was found not necessary as the pressures read by the gauges were practically constant even after continued running. If the condensing space had not been ample the pressure due to the mercury vapor would have risen after running the arc some minutes. The plan followed in these experiments was to exhaust the tube to the desired point and then cut off the pump by means of the barometric valve *b*. The gauges were cut in most of the time. These could be cut out by simply raising and clamping in position their respective mercury reservoirs.

Temperature-Pressure Relation.

In Fig. 3 are shown the temperature gradients in the region of the platinum anode for five different current strengths at an approximate constant pressure of .05 mm. mercury. The curves are all

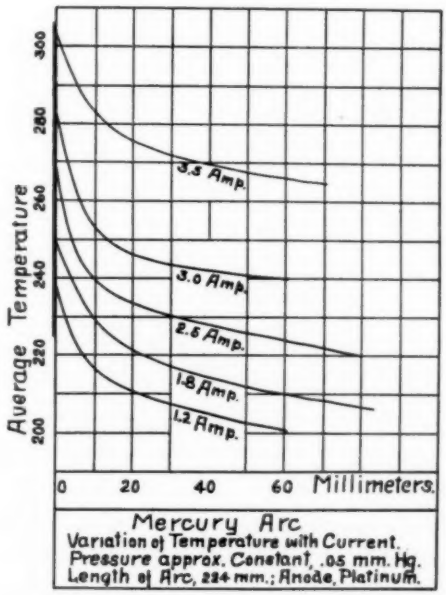

Fig. 3.

of the same general form. For a given current strength the temperature rises rapidly as the anode is approached. Again, for a given distance from the anode the temperature rises rapidly with

the current. It is interesting in this connection to construct a temperature-current curve for, say, the point 30 mm. from the anode.

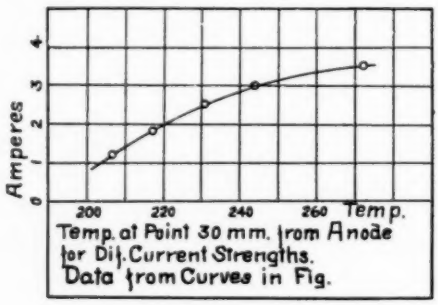

Fig. 4.

The resulting curve is given in Fig. 4, and, as we should expect, is not unlike the earlier curves given in Fig. 1.

TABLE I.

Pressure, .07 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.
38.0	236.6	9.5	252.3	6.0	260.4
28.0	238.6	6.5	255.5	11.5	249.0
23.0	242.4	3.5	267.0	18.0	242.8
18.0	243.8	1.5	277.5	28.0	238.7
13.0	245.9	1.5	277.5	48.0	235.4

An important case is to determine the thermal gradients under the condition that the pressure vary while the current be kept constant. The plan of conducting the observations was to exhaust the system to the desired pressure, close the barometric valve *b*, and cut out either the large or small gauge, or both in case the pressure rose to values higher than could be measured by either gauge. These latter pressures were read off directly by observing the mercury columns in the two legs of the barometric seal. The pressure was changed from a lower to a higher pressure by the introduction of a little air. In taking each reading ample time was allowed for the arc and junction to settle down to a steady state. It was surprising how quickly the thermo-couple took up the tem-

TABLE II.

Pressure, .083 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp in Degrees C.	Fall of Potential in Volts.
224	—	20.4	7	259.7	3.9
222	84.0	—	3.2	268.8	3.8
220	—	13.9	1.8	278.4	
216.8	95.0	—	.5	283.5	
213.4	98.5	—	.5	283.5	
210	105.0	12.4	3	267.8	
205	115.5	11.9	10	254.2	
200	140.0	11.6	27	247.8	
195	177.0	11.2	37	251.9	
185	204.2	11.4	42	252.7	
175	217.8	10.6	72	242.9	
160	229.5	9.7	95	237.5	
140	233.8	8.7	135	235.5	
115	236.5	7.7	150	234.5	
85	240.2	7.1	165	230.2	
72	245.0	6.6	175	223.9	
57	249.0	—	185	209.0	
47	247.8	—	190	196.8	
37	250.7	5.3	200	159.2	
27	251.0	5.1	205	132.6	
22	251.9	—	208	115.0	
17	252.0	4.4	211.5	104.5	
12	254.0	—	215	103.0	
9.5	255.5	—	218	97.3	
			220	94.5	

perature of the tube. Readings were taken going up to and coming down from the anode. Potential readings were also taken and these are recorded in the same tables with the temperautre values. These data are contained in Tables I. to VII. and the corresponding temperature gradients are given in Fig. 5. The length of the arc was maintained constant at 224 mm. The current was also kept constant at 3 amperes. To avoid fluctuations the usual inductive resistance (not shown in Fig. 2) was placed in the circuit.

Turning our attention to the anode we see that the curves have the same general characteristics as those given in Fig. 3, where the pressure was kept constant and the current varied, with the exception that in this case the angle of approach to the anode becomes

larger as the pressure is increased. This is very marked in the two or three upper curves, the uppermost one (no. 7) actually dips down to the anode. The observed facts relating to curves nos. 6 and 7 were: first, that the platinum anode disk glowed a dull red, and,

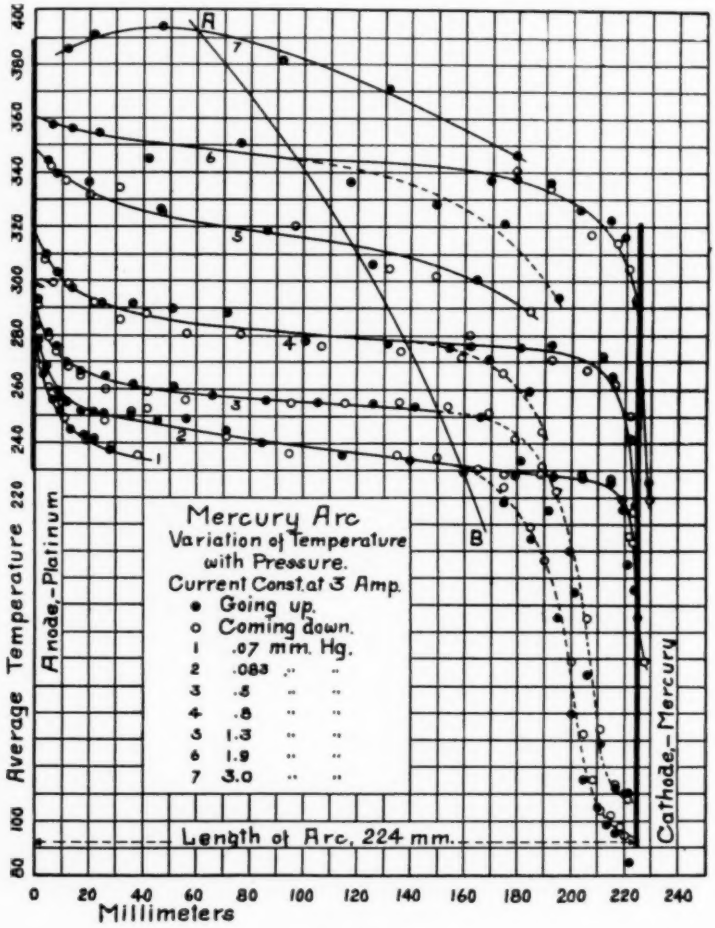

Fig. 5.

second, that the current no longer filled the tube but became stringy and flitted from side to side, seldom passing along the axis. The inference drawn from an inspection of the upper curve is that the space out from the anode was hotter than the disk itself, yet the temperature recorded was but little more than 390° C.—not nearly

TABLE III.

Pressure, .5 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.
224	—	21.0	.5	291.0	
222	110.0	14.8	4	279.3	
220	110.0	14.5	7	274.0	
217	112.5	14.4	12	268.0	
212	128.5	13.9	17	266.0	
207	154.4	13.7	27	260.0	
202	184.9	13.5	42	258.4	
192	215.8	13.3	57	256.6	
182	233.7	12.6	77	251.4	
167	249.9	11.9	97	256.6	
142	253.5	10.8	117	255.7	
127	255.0	9.8	137	256.6	
107	255.4	8.8	154	252.9	
87	256.5	7.8	169	251.8	
67	258.4	7.0	179	241.5	
52	261.2	6.3	189	232.4	
37	262.2	5.6	194	223.4	
27	265.0	5.3	199	200.8	
17	266.9	4.7	205.5	176.3	
12	270.0	4.6	212	133.9	
7	276.0	4.3	216.8	112.6	
4	281.0	4.2	221	107.5	
.5	292.5				

high enough to correspond to the dull red heat observed. This discrepancy may be explained possibly as follows: The space within the tube heats up more rapidly than the platinum disk and when the pressure is considerable the space may indeed exceed in temperature that of the anode. In other words, the temperature is not a linear function of the pressure. This is borne out by the fact that the potential difference had to be increased by more than 50 per cent. (see Fig. 13) to keep the current constant while the pressure was increased from .083 to 3 mm. of mercury. It is possible that the thermo-junction did not give the true reading, because the current no longer filled the cross-section of the tube but persisted in passing in a string-like discharge close to the walls of the tube. The fact that the temperature readings lie on so smooth a curve may be explained by the current passing at a constant distance from the

TABLE IV.

Pressure, .8 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.
224.0		22.8	8.6	303.7	4.8
223.0		16.5	4.5	310.0	4.5
219.0		16.0	3.5	308.0	
214.5		15.6	7.0	298.4	
209.0		15.3	13.8	299.0	
199.0		14.6	22.0	292.8	
184.0	259.6	14.1	32.0	285.3	
169.0	271.3	13.1	42.0	288.6	
154.0	276.0	12.6	57.0	280.2	
132.0	277.5	11.3	77.0	281.0	
102.0	278.4	9.6	107.0	276.8	
72.0	288.5	8.4	137.0	274.0	
52.0	289.9	7.3	159.0	271.4	
37.0	291.8	6.4	174.0	266.0	
25.0	292.0	5.7	189.0	244.0	
14.5	297.6	5.2			

axis—midway between the thermo-junction casing and the walls of the tube. Naturally, then, the temperature recorded would be

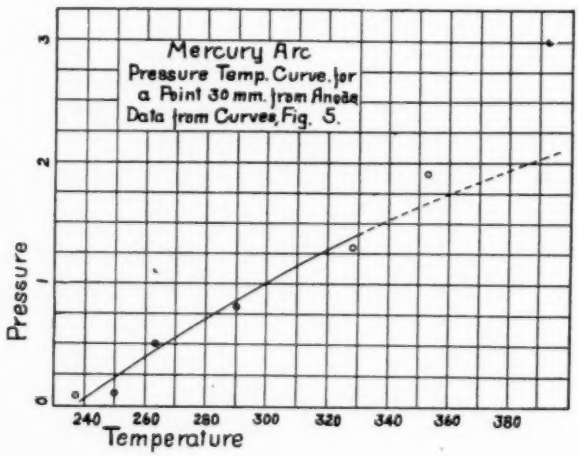

Fig. 6.

too low. This explanation is strengthened by Fig. 6 in which is given a pressure-temperature curve for a point 30 mm. from the

TABLE V.

Pressure, 1.3 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.
224.0		25.0	14.0	—	5.5
222.2		18.8	8.0	340.0	5.1
217.5		18.4	4.5	344.8	
212.5		17.4	5.1	342.6	
204.0		17.2	12.0	335.6	
189.0		16.8	20.0	332.3	
164.0	300.9	14.4	32.0	334.9	
127.0	306.4	12.8	47.0	326.2	
87.0	318.7	10.4	97.0	320.2	
47.0	326.9	7.9	132.0	304.7	
20.0	337.7	—	149.0	302.4	
28.5	—	6.5	184.0	289.2	

TABLE VI.

Pressure, 1.9 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.
224.0		27.0	117.0	337.8	—
222.1		20.1	112.0	—	13.4
221.0		19.7	99.0	—	11.7
219.0		19.6	77.0	351.8	10.9
214.0		19.3	42.0	345.5	7.8
204.8		18.9	23.0	354.5	6.4
194.0	293.3	18.1	14.0	356.0	—
174.0	321.0	16.2	7.0	357.3	5.1
149.0	328.0	15.3			

TABLE VII.

Pressure, 3 mm. Hg; Current, 3 Amperes.

Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.	Distance from Anode in mm.	Average Temp. in Degrees C.	Fall of Potential in Volts.
224	—	31.7	47	394.0	10.3
179	346.2	20.2	22	391.4	—
132	370.9	16.3	12	386.0	5.9
92	382.0	13.8			

anode. A smooth curve fits the first five points while the upper two are considerably off as explained above.

The temperature as recorded by the thermo-junction in the region of the cathode is interesting. The influence of the comparatively cool mercury surface was noticeable at a considerable distance from the cathode. It was in the main due to two causes, the cooling effect of the large mass of mercury that constituted the barometric leg, and the conduction of heat away from the thermo-junction by the wires leading to the same. This cooling effect is a linear function of the pressure and hence was least when the pressures and consequent temperatures were least. In curve 2, Fig. 5, it extended about one third way up the tube while in curve 7 it extended more than three fourths the entire length of the arc. The curve AB is drawn through the points on the temperature gradients where this cooling effect began. As drawn it is not a straight line, however it would be approximately straight if the curves 6 and 7 were not in error as was just explained.

Fig. 7.

Curves 2 and 3 indicate that the temperature of the mercury surface was about 100° C. This is in error, as stated above, because of the abstraction of heat from the couple by conduction along the wires.

To correct in part for this cooling effect, the glass casing containing the thermo-junction was bent back on itself as shown in Fig. 7. It was so bent that approximately the same length of wire was exposed to the arc when the tip was lowered to the cathode surface as when formerly it was raised to the anode. The cathode end of curves 2, 4 and 6 were thus corrected. The data are given in Table VIII. Attention should be called to the smoothness of the corrected curves. Some lack of symmetry was to be expected since it was necessary to let the vacuum down and remove the glass capillary for bending and later to again exhaust the system to the proper degree. In the three corrected curves the error due to the cooling effect of the mercury surface is still present. The dip of the curve as it approaches the cathode could be lessened by using a smaller quantity of mercury, and at the same time more nearly isolating it.

TABLE VIII.

Current, 3 Amperes.

Pressure, .083 mm. Hg.		Pressure, .8 mm. Hg.		Pressure, 1.9 mm. Hg.	
Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.
221.5	195.5	224.0	217.2	265.5	124.5
223.5	186.1	222.1	241.8	229.5	226.0
219.0	216.0	214.5	264.1	224.0	291.7
214.0	226.0	211.5	272.1	219.5	317.2
204.0	227.0	192.3	277.8	214.5	322.5
193.0	228.0	180.5	276.8	204.5	327.0
179.0	228.1	162.5	276.8	192.0	337.0
189.0	228.1	162.5	280.2	179.5	337.8
204.0	228.1	180.5	285.3	169.5	337.0
214.0	227.0	192.3	270.5	162.5	344.9
219.0	219.4	206.5	267.8	179.5	340.5
221.5	205.5	216.5	261.2	192.0	335.0
223.5	203.0	222.2	250.0	205.5	317.3
224.2	177.6	223.5	215.0	216.5	314.2
227.0	159.2			220.7	304.8
				223.7	291.9
				229.5	219.0
				265.5	126.0

TABLE IX.

Pressure, .083 mm. Hg; Current, 3 Amperes.

b. Along a Diameter 27 mm. from Anode.		*c.* Along a Diameter 137 mm. from Anode.	
Distance from Axis of Tube in mm.	Average Temp. in Degrees C.	Distance from Axis of Tube in mm.	Average Temp. in Degrees C.
0.0	253.7	0.0	234.5
1.3	250.7	1.0	233.6
3.0	243.7	3.5	220.5
4.0	233.3	7.5	203.1
6.0	224.7	10.5	180.5
8.5	216.0		
10.0	213.0		

It is quite possible that many of the irregularities in the position of the points making up the curves in Fig. 5 are due to a failure to properly center the thermo-junction as it was moved along the axis of the tube. This was investigated by Geiger[1] for the case of dis-

[1]Ann. d. Physik., IV., F, Vol. 22, p. 1001, 1907.

charge through gases. He found that in a tube 37 mm. in diameter the temperature along the axis was 238° C. while at the inner side of the wall of the tube it fell to 149° C. To test this point for the case of the mercury arc temperature readings were taken along a diameter at two different positions in the tube just after the data for curve 2, Fig. 5, were collected. The first position was at a distance of 27 mm., and the second at a distance of 137 mm. from the anode. The temperatures are recorded in Table IX. In Fig. 8 are shown three curves. Curve *a* (no. 2 above) is the temperature gradient along the axis, while curves *b* and *c* are the gradients in

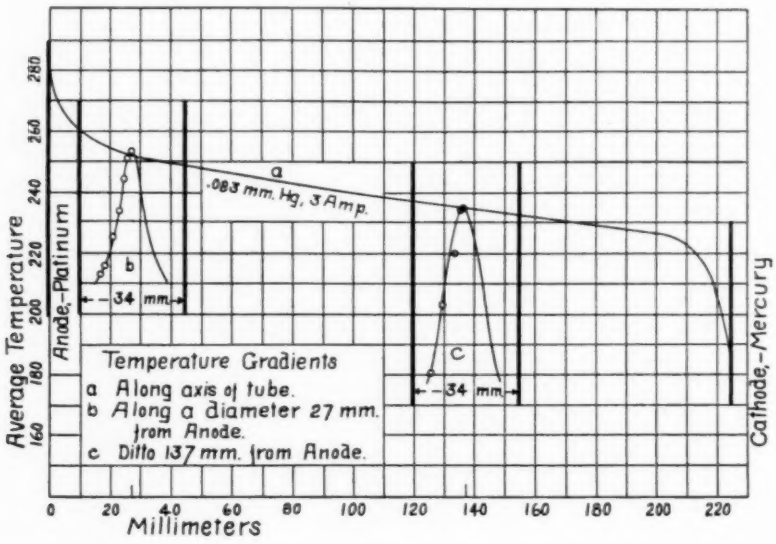

Fig. 8.

question. The length of the tube, its diameter and the respective distances of *b* and *c* from the anode are shown drawn to scale. The curves *b* and *c* show that the temperature falls off very rapidly as you leave the center and in this particular case was as much as 20 per cent. of the whole at a distance of 12 mm. from the axis.

It was suggested that the reading of the junction would be largely affected by the nature of the surface of the glass casing enveloping the same. To test this point the glass casing was removed (Fig. 7) and straightened out as originally used. After reassembling and

adjusting the pressure and current, temperature readings were taken in the region of the anode with the casing clear. The casing was then again removed and the bulb containing the couple was blackened (as also was 3 or 4 cm. of the stem) by holding it in a red gas flame. The blackened casing was then carefully replaced in the tube MN and the exhaustion again pushed to .05 mm. mercury when the arc was started. The current as before was kept constant at 3 amperes. The lampblack adhered quite well and did not seem to interfere with the action of the arc. It, however, soon began to burn off the casing nearest the cathode, and by the time the run was completed it had disappeared pretty well from the lower side of the bulb—the side exposed to the cathode discharge. A rather strange phenomenon was observed at this stage. It was noticed that a small flame lit on the platinum tip (Fig. 9, *a*) and grew in size as the $T-J$ was lowered. As it passed the opening N the flame leaned over toward the exhaust nipple and when slightly below it a spark flew off the flame and entered N going out as it moved up the tube. The flame became erect again and symmetrical about the tip when it was lowered farther. As the bulb approached the cathode another spark left the flame and rose rapidly tracing a wavy path as though it were passing through air. Later, on closer observation, a flame was to be seen on the glass casing (Fig. 9, *b*) opposite the opening N. As the casing was moved up or down the flame seemed to glide along the surface of the glass. By jarring the apparatus slightly it at times could be shaken off and would invariably enter the nipple N. This was noticed only when there was lampblack present. The casing was next entirely freed of lampblack by lowering it to the region of the cathode and allowing the same to be burned off; however, its presence was now evident on the surface of the mercury. The run was then repeated with the bulb clear.

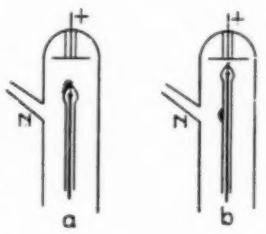

Fig. 9.

The data for these three runs are contained in Table X., and the same are plotted in Fig. 10. The inference from the curves naturally is that the temperature readings were quite independent

of the nature of the radiating surface surrounding the thermo-junction.

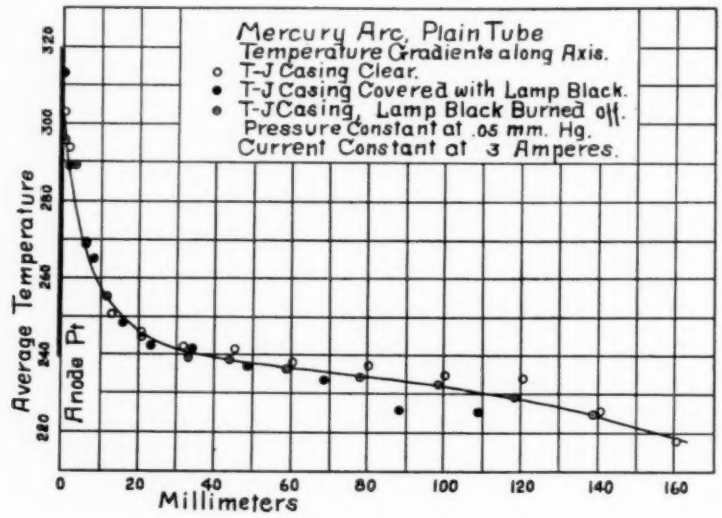

Fig. 10.

TABLE X.

Plain Tube; Pressure, .05 mm. Hg; Current, 3 Amperes.

T-J Casing Clear.		T-J Casing Covered with Lampblack.		T-J Casing, Lampblack Burned Off.	
Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.	Distance from Anode in mm.	Average Temp. in Degrees C.
.5	303.2	.5	314.3	.5	296.0
1.5	293.0	1.5	288.5	2.5	288.6
5.5	268.3	8.5	264.6	2.5	268.6
12.5	250.6	15.5	247.7	12.5	254.6
20.5	246.8	23.5	242.2	20.5	244.9
32.5	242.0	33.5	241.8	33.5	239.0
45.5	241.8	48.5	237.5	43.5	238.2
60.5	238.6	68.5	233.0	58.5	236.7
80.5	237.0	88.5	226.0	78.5	233.4
100.5	234.5	108.5	225.0	98.5	231.4
120.5	232.9			118.5	228.5
140.5	225.0			138.5	223.5
160.5	218.0				

To still further test this point a hooded tube with a ring mercury anode and an annulus mercury cathode was ordered of the form shown in Fig. 11 and the three runs under conditions similar to those above were repeated. The pressure as before was .05 mm.

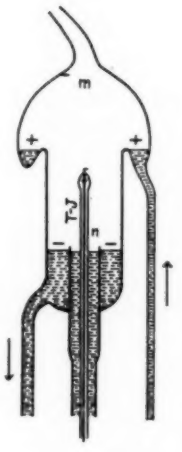

Fig. 11.

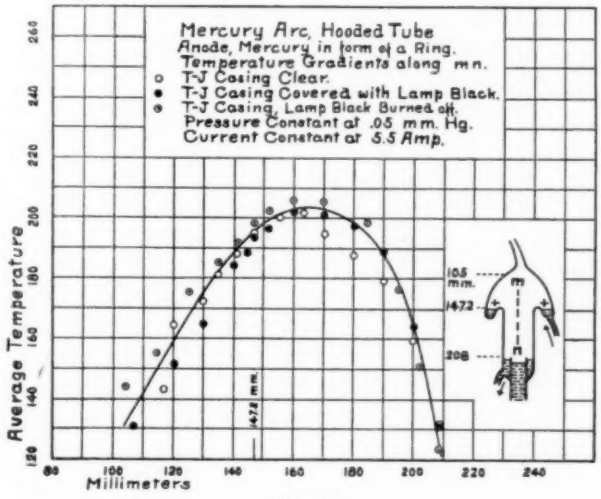

Fig. 12.

mercury and the current was adjusted to the same density. Again the data (Table XI.) when plotted (Fig. 12) show that the thermo-junction readings were practically the same whether the surface of the casing was a good absorber or a good reflector of radiation falling upon it.

Potential-Pressure Relation.

The potential gradient along a discharge tube containing gases at low pressures has engaged the attention of investigators[1] for a number of years. The potential-pressure relations for the particular case of the mercury arc has been investigated by Heuse[2] and Pollak.[3] The latter measured the potential gradient along the arc in a vertical tube by means of a movable electrode and an electrometer. His apparatus was constructed with great precision. He did not, however, investigate the potential gradient for different pressures.

[1]Thomson, J. J., Conduction of Electricity through Gases, p. 555.
[2]Heuse, Ann. d. Physik., Vol. V., p. 678, 1901.
[3]Pollak, J., Ann. d. Physik., Vol. 19, Feb. 8, 1906.

TABLE XI.

Hooded Tube; Pressure, .05 mm. Hg; Current, 5.5 Amperes.

T-J Casing Clear.		T-J Casing Covered with Lampblack		T-J Casing, Lampblack Burned Off.	
Distance Along Axis of Tube in mm.	Average Temp. in Degrees C.	Distance Along Axis of Tube in mm.	Average Temp. in Degrees C.	Distance Along Axis of Tube in mm.	Average Temp. in Degrees C.
208.0	132.0	208.0	130.8	208.0	123.0
200.0	159.0	200.0	163.6	202.0	150.2
190.0	178.8	190.0	188.9	195.0	176.3
180.0	187.6	180.0	197.5	184.0	198.0
170.0	194.4	170.0	200.7	170.0	205.0
163.2	202.4	160.0	201.0	160.0	206.0
155.0	200.0	152.0	196.2	152.0	202.5
147.2	194.5	147.2	193.0	147.2	198.0
140.5	188.3	144.5	188.4	141.6	191.8
134.5	181.1	140.0	183.8	135.0	184.2
130.0	171.8	130.0	164.4	125.0	174.7
120.0	163.3	120.0	152.0	114.0	155.0
117.0	143.2	107.0	130.8	104.0	143.2

In Fig. 13 are plotted the potential readings between the anode and the movable exploring electrode *T–J*, Fig. 2, contained in Tables I. to VII. The pressure was varied from .083 to 3 mm.

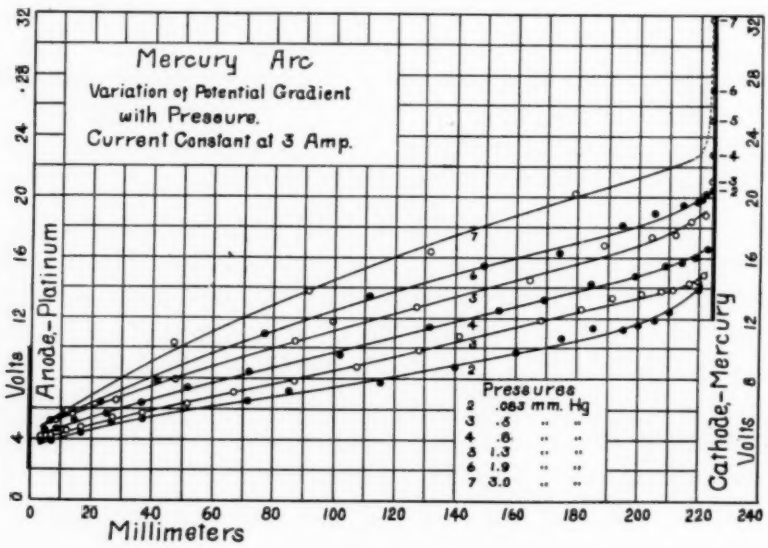

Fig. 13.

mercury, and was, as stated before, due to the presence of air and not to an excess of mercury vapor. The current was kept constant at 3 amperes. It will be noticed that the potential gradient in the positive column increases with the pressure. The general form of any one curve is the same as that obtained by Pollak. The anode drop is nearly the same for the range of pressures used. The anode drop is smaller than the cathode fall, however the rate of increase with pressure is not the same. The anode drop increased approximately one volt over the range of pressures used while the cathode fall increased by approximately 3 volts.

The potential gradients for various distances from the anode is shown plotted against pressures in Fig. 14. The increase is small near the anode but becomes more as the cathode is approached.

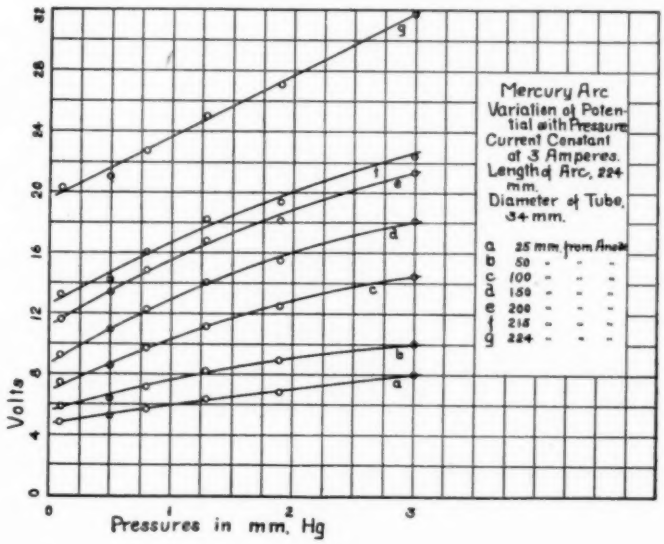

Fig. 14.

Curves a and g are linear. To them the characteristic relation $v = a + bp$, where p is the pressure and a and b constants, would apply.

SUMMARY.

The average temperature of the mercury arc in a vertical tube was investigated from electrode to electrode by means of a movable

thermo-junction introduced through the barometric leg of the lamp for pressures up to 3 mm. mercury at a constant current of 3 amperes.

The temperature increased very rapidly with the pressure,—even more rapidly than the data obtained would indicate since for high pressures the current became stringy and it was impossible to get true readings.

It was also pointed out that the cooling effect may readily mask the temperature readings. In this particular instance this effect was due to the comparatively cool mercury surface forming the cathode, also to the conduction of heat away from the junction by the wires. Three temperature curves were corrected.

The temperature gradient along a diameter 27 mm. from the anode showed a fall in temperature of 20 per cent. of the whole at a distance of 12 mm. from the axis in a tube 34 mm. in diameter.

The temperature readings were shown to be approximately independent of the nature of the radiating surface enclosing the thermo-junction.

Potentials were also read simultaneously with the temperature readings, and the resulting potential-pressure curves indicated that the relation is approximately linear.

Acknowledgment is due Mr. W. W. Stifler for assistance rendered.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
April, 1910.

SOME OBSERVATIONS ON THE SILENT DISCHARGE THROUGH AIR.

By Dicran H. Kabakjian.

WHEN two electrodes separated by an air space are gradually raised to a high difference of potential and watched in a darkened room it will be observed that before the sparking takes place there is a silent discharge at the edges of the electrodes, especially if there are any sharp points on them. It is also well known that ozone is formed near these points of discharge. It is not easy, under ordinary circumstances, to obtain a steady discharge, in this way, for any length of time without sparking, as the high state of ionization of the air and also the presence of the vapor of the electrode material facilitate the passage of sparks or the formation of an arc between the electrodes.

A steady silent discharge, however, can be easily obtained if one or both of the electrodes are covered by thin sheets of an insulating material, such as glass or mica, and an alternating E.M.F. of suitable voltage is applied to them. As the insulating material excludes the vapor of the electrode materials from the air space, large variations in the current density can be obtained without any danger of sparking or arcing so long as the voltage is not high enough to break through the insulators.

The writer has made some observations into the nature and properties of such a discharge under varying circumstances, in connection with his study of the ozone formation by silent discharge, the results of which are given in a separate paper.

The discharge was obtained between tin-foil electrodes mounted on glass disks. One of the electrodes was always covered by a thin sheet of glass or mica, and an alternating E.M.F. of 60 cycles which was stepped up to the desired voltage by means of a transformer, was applied to their terminals.

The curve in Fig. 1 shows the building up of the current in such

an arrangement as the voltage is gradually increased. The dielectric is a single mica disk 0.05 mm. in thickness, covering one of the electrodes. The distance between the electrodes is 1 mm. It will be seen that the current is very small until the voltage reaches the discharge point, when it suddenly builds up, increasing with the increase in voltage although not at constant rate.

An oscillographic examination of the silent discharge showed it to vary in nature under varying conditions, such as increasing or decreasing the air space and the capacity of the ozonizing apparatus. The oscillograph used was one made by the General Electric Com-

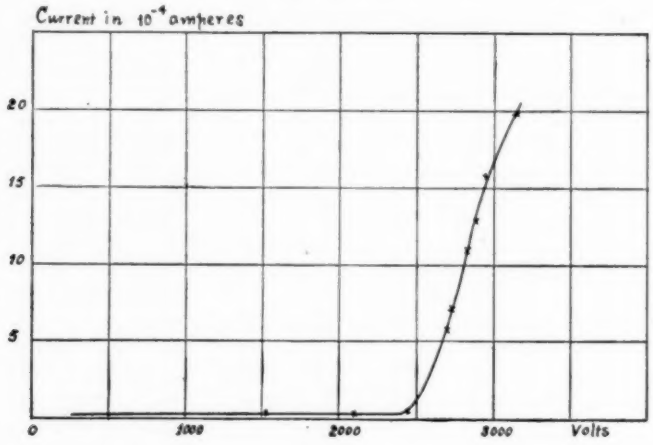

Fig. 1.

pany and its vibrating systems had a maximum sensibility of 8 mm. deflection for a current of 0.005 ampere.

As the current which could be obtained from the apparatus designed for the study of ozonization by the silent discharge was necessarily rather small, some difficulty was entertained in obtaining a point of light small enough to give a sharp image of the current curve and at the same time bright enough to make a fairly distinct impression on the film. Figs. 2, 3 and 4 (see Plate) were obtained from circular tin-foil electrodes mounted on glass disks.[1] One of the electrodes was covered by a mica disk of 0.05 mm. thickness. The

[1]For the details of the apparatus see the description of the ozonizer in the writer's article on "The Formation of Ozone by Silent Discharge." PHYS. REV., 31 (1910), p. 122.

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FIG. 2.

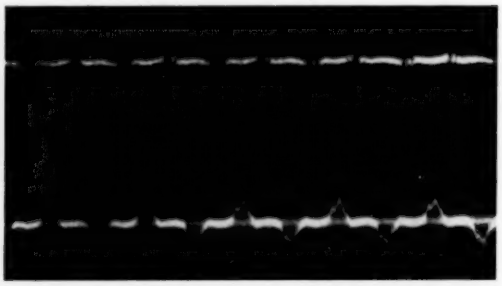

FIG. 3.

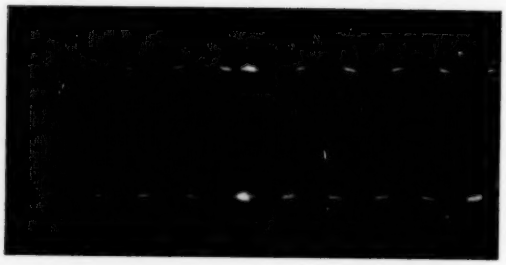

FIG. 4.

FIG. 5.

FIG. 6.

KABAKJIAN

The Silent Discharge in Air

radius of the foils was 2.40 cm. and that of mica 3 cm. A current of dry air was made to flow between the electrodes while the discharge was passing.

All the figures were obtained by connecting one of the vibrating systems of the oscillograph in series with the dischrage electrodes. The zero line was obtained by giving the film a second exposure immediately after the first one but without any current.

Fig. 2, *a*, shows the current curve when the air-space was 1.6 mm. The discharge was unsteady in appearance and noisy, and the curve shows it to consist of highly damped oscillations of more or less irregular form. It will also be noticed that the curve is not symmetrical with reference to its zero line. The current used was 0.00272 ampere.

In *b*, Fig. 2, the air-space was reduced to 1 mm.; the oscillations are seen to diminish in number and also in amplitude, and the curve is more regular in form.

Still more decreasing the air space gave a better curve still as is seen from Fig. 3, where the air-space was only 0.5 mm.

Fig. 3, *a*, was obtained with a non-inductive resistance of 33,000 ohms in series with the electrodes and *b* with this resistance cut out. The curves are almost exactly alike, showing that inserting such a resistance in series does not appreciably alter the form of the discharge curve.

Fig. 4 was obtained with the same apparatus with an air-space of 0.27 mm. only. These figures show that with decreasing air-space the curves become smoother and approach more and more a sine curve. The effective value of the current used in all these curves was the same, *i. e.*, 0.00272 ampere.

Fig. 5 was obtained by a modified form of apparatus. The electrodes consisted of ten pairs of rectangular tin foils 5.5 × 3 cm. in area mounted on glass plates and arranged in parallel with 0.5 mm. air-space between them. One electrode of each pair was covered with a mica sheet 0.05 mm. in thickness, the other being bare as before. The value of the current in Fig. 5, *a*, was the same as the above while that in *b* was 0.0045 ampere.

Fig. 6 was obtained from discharges between wire gauze electrodes separated by glass. A common test-tube 2.5 cm. in diameter and

20 cm. in length was covered inside and outside by fine brass gauze to a distance of 2.5 cm. from each end, forming a cylindrical condenser. This fitted loosely into a glass tube drawn out at one end and a smaller test-tube was fitted inside. The end of the outer tube was connected to an aspirator and a current of air passed over the electrodes. When the electrodes were connected to a difference of potential of 3,500 volts a luminous silent discharge took place between them. The air drawn out at the other end contained much ozone, and the arrangement worked as a good ozonizer.

The figure shows a smooth discharge curve which is to be expected considering the fact that the air space was exceedingly small and the capacity was large compared with the cases where only one pair of small electrodes were used as in Figs. 2, 3 and 4.

The curve *a* in Fig. 6 corresponds to a current of 0.00272 ampere, while *d* was obtained with one of 0.004 ampere. Both these and the curves of Fig. 5 show that the current density per square centimeter does not appreciably change the form of the discharge curve, this apparently depending upon the relation between the air space and the capacity.

The Effect of Moisture.—The presence of considerable water vapor has a marked effect both on the appearance of the discharge and also on the value of the current passing through the gas for a given potential difference.

Although the leakage current is always greater for the same potential difference and the same air space with moist air than with dry before the discharge point is reached, the reverse takes place when the discharge is established, that is, the discharge current is smaller for moist air than for dry, under similar circumstances.

The appearance of the discharge in the two cases is also different. With dry air it is in the form of a diffused glow while with moist air it is concentrated at isolated points and presents the appearance of a large number of tiny sparks scattered over the surface of the dielectric disk.

The presence of moisture also greatly diminishes the luminosity of the discharge. This was demonstrated in the following way. Both electrodes were covered with thin sheets of mica and a disk of brass wire gauze was inserted between them. The electrodes

were then pushed towards each other as far as they would go, the mica sheets making good contact with the surface of the wire gauze. The voltage was adjusted to give a weak luminous discharge with a current of dry air passing over the gauze. If now a current of moist air was drawn through, the value of the current fell and the luminosity completely disappeared. It could be restored, however, by drawing a current of dry air over the gauze for a short time. The effect was very prominent if the air was saturated with moisture by drawing it through water.

Zeleny has discovered the same effect in case of spark discharges.[1] He found that the presence of moisture in the air diminished the value of the current passing through it for a given voltage.

It seems probable that the effect is due to the condensing of water vapor on the ions thereby diminishing their velocity and hence decreasing their power of producing fresh ions by collisions.

The points observed can be summarized as follows.

1. A silent discharge obtained by an alternating E.M.F. and an insulating dielectric between the electrodes separated by an air space is, under certain conditions, oscillatory in character.

2. Increasing the capacity of the system or decreasing the air space tends to decrease the amplitude of these oscillations, giving rise to smoother discharge current curves.

3. Variations in current density or the insertion in the circuit of a resistance of the order of 33,000 ohms do not seem to affect the shape of the discharge curve.

4. Moisture in the air diminishes the value of the discharge current, for a given voltage and air space, as well as its luminosity.

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UNIVERSITY OF PENNSYLVANIA,
NOV. 18, 1909.

[1]See PHYS. REV., 26, pp. 448–463, June, 1908.

THE FORMATION OF OZONE BY SILENT DISCHARGE.

BY DICRAN H. KABAKJIAN.

THE different methods of the formation of ozone by means of a silent electric discharge through air or oxygen have been investigated by various writers. The formation of ozone by means of a brush discharge from sharp points has been exhaustively studied by Professor Warburg and others in his laboratory.[1] The yield per kilowatt hour by this method was comparatively small, never reaching that obtained by the use of a dielectric between the electrodes.

A. W. Gray[2] using a modified form of Siemens type of ozonizer and an influence machine, found that the amount of ozone per coulomb increased as a linear function of potential difference. It would seem from his results that the amount of ozone produced was proportional to the energy consumed in the apparatus.

A. W. Ewell,[3] using an ozonizer with parallel plate conductors one of which was covered with a sheet of glass, and an alternating current of 6,000 to 30,000 volts, found the amount of ozone produced per coulomb to be a function of current density through the gas, reaching a maximum and then rapidly falling off with the increase of the current. This fact was explained by him as due to the deozonizing effect of the current pointed out by Warburg.[4] No direct relation can be obtained from his results between the energy consumed in the ozonizer and the amount of ozone produced by the discharge.

APPARATUS.[5]

A cylindrical glass tube 3.5 cm. in length and 3.25 cm. in radius was fitted with a square brass plate at one end and a glass plate at

[1]Verhandl. d. Deutschen Phys. Gesellsch., 22, p. 382, 1903. Preuss. Akad. Wiss. Berlin Sitz. Ber., 46, pp. 1011–1015. Annalen der Phys., 17, 1905, pp. 1–30, etc.

[2]PHYS. REV., Nov., 1904, pp. 347–368.

[3]PHYS. REV., 22, 1906, pp. 232–244.

[4]Ann. der Phys., 9, p. 788, 1902.

[5]This apparatus, which is not essentially different from the one used by Ewell, was constructed by the writer before he had seen the results of Ewell's investigation, the article having somehow escaped his notice.

the other, which, when bolted together by means of brass rods passing through the corners and sealed with wax at the outer edge of the cylinder, formed a small air-tight chamber. A glass disk *a*, Fig. 1, 3 cm. in radius was mounted on one of these plates and carried one of the electrodes. A similar disk *b* parallel to the first one, attached to a movable brass rod *c* passing through the center of the brass plate, carried the other electrode. The brass rod *c* was provided with a screw drive and a graduated screw-head *d* by means of which the distance between the electrodes could be varied and accurately determined. The electrodes were tinfoil disks 2.5 cm. in radius, one of which was always covered with a disk of glass or mica 3 cm. in radius and of various thicknesses, cemented to the electrode by means of shellac solution.

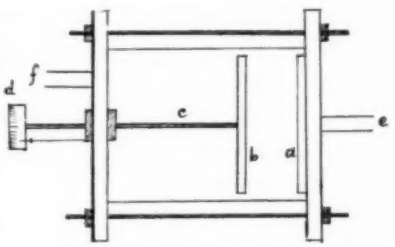

Fig. 1.

A glass tube *e* passing through the center of the glass plate and cemented to it with shellac, was ground to fit a hole at the center of the glass disk *a* carrying the stationary electrode. The air entered the chamber through a brass tube *f* and after passing radially through the space between the two electrodes, where the discharge took place when the ozonizer was in action, left through the glass tube *e* at the center.

The volume of the air drawn through was measured by a gas meter in the circuit. It was dried by passing through concentrated sulphuric acid and a long glass tube filled with alternate layers of glass-wool and fresh phosphorus pentoxide. Another glass tube filled with cotton-wool served to retain any particles that might be carried by the air just before it entered the ozonizer (see Fig. 2). On leaving the ozonizer the air passed through two wash-bottles containing pure distilled water to take up any oxides of nitrogen, then through two more such bottles containing potassium iodide solution (about 0.5 gm. KI in 500 c.c. of water) and through a flask of 2.5 liters capacity, to equalize sudden changes in pressure, to the aspirator. The wash-bottles had ground glass stoppers and in

making the connections great care was taken to reduce to a minimum the contact of ozonized air with any oxidizable substances.

An alternating current of 60 cycles and 110 volts was stepped up by means of a transformer to the desired voltage, which was measured by means of an electrostatic voltmeter constructed for this purpose and calibrated by means of a Kelvin multicellular voltmeter. The effective value of the current was determined by reading the fall of potential across a non-inductive carbon film resistance (20,000–80,000 ohms) by means of a Kelvin voltmeter.

The amount of ozone produced by the discharge was measured in the following way. The aspirator was adjusted until it gave a

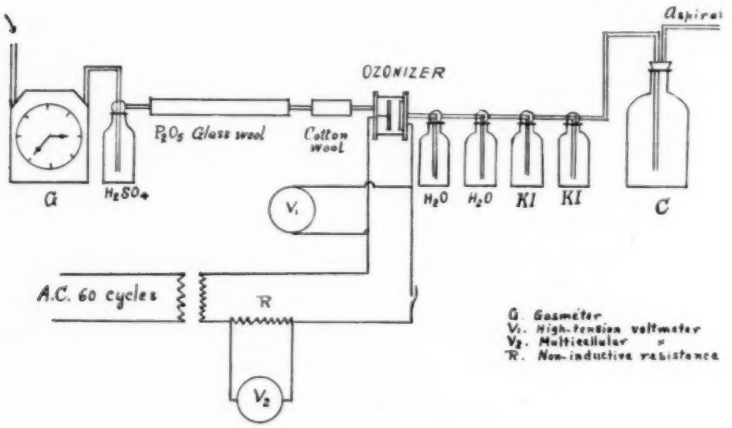

Fig. 2.

desired air current of approximately constant velocity.[1] The current was turned on for one minute and then cut off. When enough air had passed through to replace the air in the apparatus, the wash-bottles containing the iodide solution were disconnected, acidified and the liberated iodine determined by titrating with fresh thiosulphate solution.

The titrated solutions were kept for one or two hours to test for any recoloration, the absence of which proved[2] that all the oxides of nitrogen had been absorbed before the ozonized air reached the iodide solutions.

[1]Small variations in the velocity of the air current made no appreciable difference in the production of ozone.

[2]Ann. der Phys., 17, 1905, p. 22.

Ewell concludes from his investigation that the amount of ozone produced per coulomb depends upon the current density. But since the current per square centimeter passing through the gas for a given voltage and air space depends also upon the capacity of the ozonizer, it would be of interest to note the effect of varying the capacity on the yield of ozone per coulomb. This was done both by varying the thickness of the dielectric between the electrodes and the air space between them. The results of these variations are given below.

Variation of Air Space.

To determine the effect of varying the air space on the yield of ozone per coulomb the following measurements were taken. Tables I. and II. were obtained by using a mica disk 0.2 mm. in thickness,

Table I.

Dielectric, mica, 0.2 mm. d = 0.15 mm.

No.	V	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	1,380	194	62	5.54
2	1,850	355	155	7.27
3	2,760	584	341	9.70
4	3,270	740	418	9.40
5	4,750	1,090	620	9.50
6	5,350	1,220	728	9.90

Table II.

Dielectric, mica, 0.2 mm. d = 1.0 mm.

No.	V	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	2,300	165	201	20.3
2	2,660	335	526	26.2
3	3,050	426	651	25.5
4	3,390	489	929	31.7
5	4,520	745	1,510	32.9
6	5,400	1,020	2,030	32.7

and III., IV. and V. with a glass disk 1 mm. in thickness. These disks were always cemented on the same electrode. Velocity of the air current was 1.2 liters per minute.

In these tables d is the air space in millimeters, V is the difference

of potential in volts, i the current in amperes, O the mass of ozone produced in grams per minute, and Y the yield per coulomb in grams. In Tables III., IV. and V. the voltage is not given as in some of the readings it was beyond the range of the voltmeter used.

TABLE III.

Dielectric, glass, 1.0 mm. d=0.6 mm.

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	150	198	22.0
2	206	305	24.6
3	281	442	26.2
4	370	602	27.1
5	470	808	28.6
6	572	1,070	31.1
7	640	1,220	31.8

TABLE IV.

Dielectric, glass, 1.0 mm. d=1.6 mm.

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	196	352	29.9
2	228	527	38.5
3	290	718	41.0
4	360	938	43.4
5	385	1,055	45.6
6	442	1,235	46.4
7	518	1,470	47.1
8	588	1,730	49.0

TABLE V.

Dielectric, glass 1.0 mm. d=3.2 mm.

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	255	835	54.6
2	297	1,010	59.3
3	375	1,360	60.6
4	400	1,440	60.4
5	445	1,540	55.0
6	493	1,760	59.4

The examination of these figures at once shows that the yield per coulomb is greatly increased with the increase in air space and

hence decrease in capacity. For example, when mica is the dielectric, an increase of air space from 0.15 mm. to 1 mm. increases the yield more than three times, while in the case of the glass disk increasing the air space from 0.6 mm. to 3.2 mm. more than doubles the yield per coulomb.

To test if an increase in capacity by simply increasing the area of conducting surface would produce the converse effect, an ozonizer was constructed of six rectangular glass plates 5×6.7 cm. and about 1 mm. thickness and on one side of each of these, rectangular pieces of tin foil 3×5.5 cm. were pasted. The plates were arranged in parallel with about 1 mm. of air space between, through which the air current was made to pass, the rest of the arrangement being the same as before.

The measurements are given in Table VI. Comparing these with the figures of Tables III., IV. and V., in which glass of the same thickness was used as the dielectric, it will be readily seen that the maximum yield in this case is always smaller than any one of them although the air space is greater than one and less than the other two.

TABLE VI.

Six plates. Dielectric, glass, 1.0 mm. $d = 1$ mm.

No.	V	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	2,230	243	87	6.08
2	2,460	333	338	18.30
3	2,620	460	654	23.7
4	3,150	691	1,005	25.2
5	3,460	770	1,265	27.4
6	4,140	916	1,500	27.2
7	4,640	1,150	1,920	27.8
8	5,400	1,460	2,490	28.4

In the curves plotted in Fig. 3 and Fig. 4 the abscissæ are the values of current in 10^{-4} amperes and the ordinates ozone produced per minute in 10^{-4} grams.

It will be seen that except at the start all the curves are very nearly straight lines, showing that at those parts the mass of ozone produced in each is almost a simple linear function of the current, independent of the voltage, although the amount produced by the

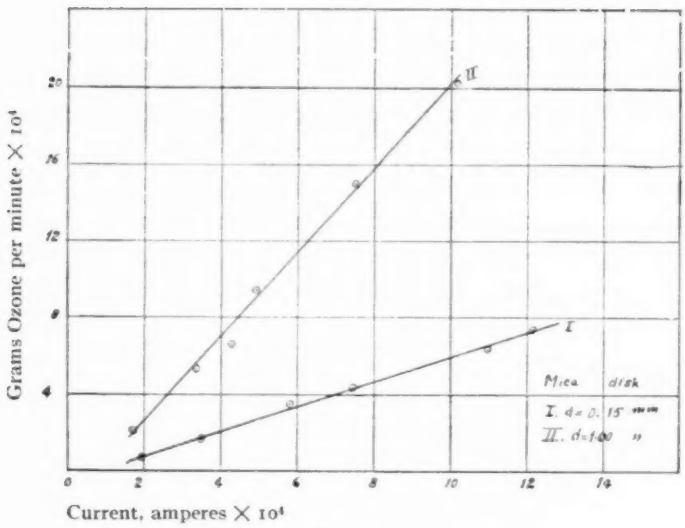

Fig. 3.

same current is different in different cases depending upon the constants of the arrangement such as air space, capacity, etc., and is greatest where the capacity is smallest.

In Fig. 5 curves are plotted to show the relation between the yield

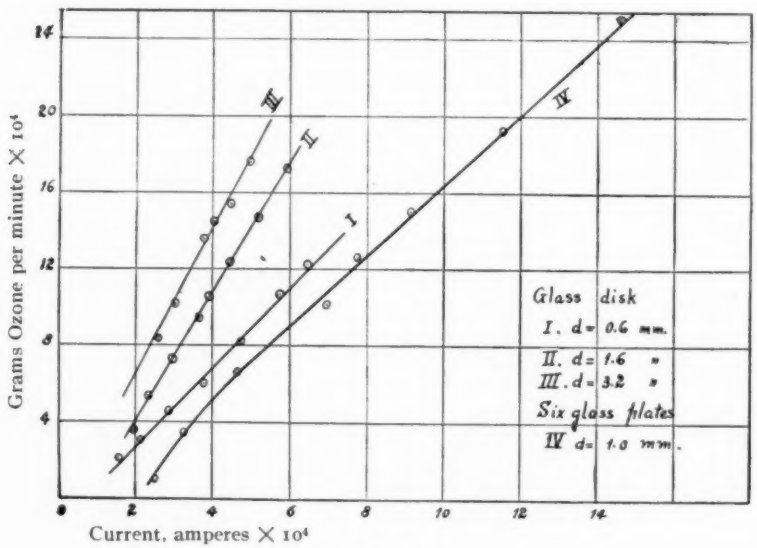

Fig. 4.

per coulomb and the voltage. The abscissæ are the difference of potential in volts and the ordinates the mass of ozone per coulomb in milligrams. Curves I. and II. are taken from readings in Tables I. and II., while curve III. is from Table VI. The curves all indicate a more or less steep rise at the start, but soon tend to become parallel to the axis of abscissæ, showing that beyond a certain point the additional increase in voltage has very little effect on the yield per coulomb. The maximum yield and the value of the voltage at which this maximum is reached, however, is very different in different curves.

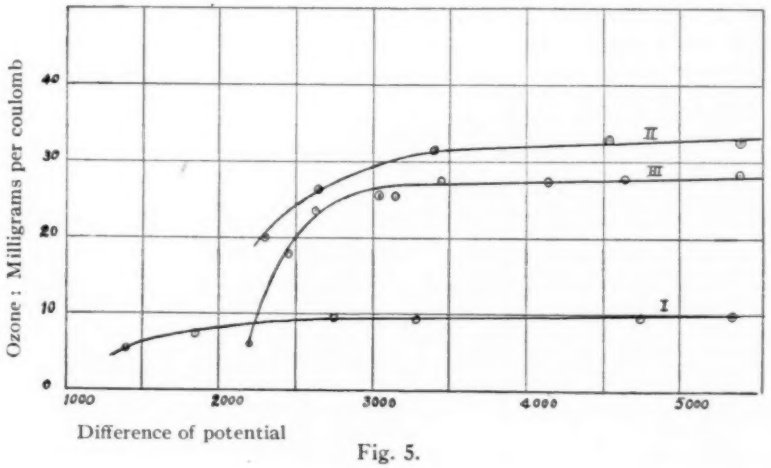

Fig. 5.

Variation of the Thickness of the Dielectric.

The effect of variation in capacity by simply varying the thickness of the dielectric plate, keeping everything else unchanged was also examined. Three discs of the same radius but of different thicknesses were used for this purpose. No. 1 was of mica .04 mm. in thickness, no. 2 also mica .20 mm. in thickness, while no. 3 was of glass 1 mm. in thickness.

The readings were taken in as nearly similar conditions as possible. The results are given in Tables VII. and VIII.

These figures show that for the same air space and current density the yield of ozone per coulomb for different thicknesses of the dielectric is in the direct order of the thickness and consequently

TABLE VII.

$d = 0.6$ *mm.*

No.	Dielectric.	V	$i \times 10^6$	$O \times 10^6$	$V \times 10^3$
1	mica .04 mm.	1,950	450	390	16.7
2	" "	2,050	580	643	18.5
3	" "	2,250	810	935	19.7
4	" "	2,570	1,230	1,850	25.1
5	mica .20 mm.	2,530	420	643	25.5
6	" "	2,900	504	838	27.8
7	" "	3,700	679	1,010	26.8
8	" "	4,750	988	1,770	29.6
9	" "	5,500	1,180	2,180	30.8
10	glass 1 mm.		390	605	25.8
11	" "		458	877	31.9
12	" "		611	1,210	33.0

TABLE VIII.

$d = 1$ *mm.*

No.	Dielectric.	V	$i \times 10^6$	$O \times 10^6$	$V \times 10^3$
1	mica .04 mm.	2,800	550	916	27.8
2	" "	3,050	840	1,750	34.8
3	" "	3,450	1,470	3,060	34.7
4	mica .20 mm.	3,550	550	1,270	38.4
5	" "	4,880	840	2,240	44.5
6	" "	6,850	1,470	3,590	40.7

in the inverse order of the capacity, although the effect in this case is not so marked as in the case of increased air space.

The results already obtained show that the quantity of ozone produced in an ozonizer for a given current is closely related to the capacity of the ozonizer, and hence to the energy consumed in the circuit. The increase in the yield per coulomb by decreasing the capacity does not necessarily mean an increased efficiency, since the voltage necessary to give a certain current in the gas is much higher in the latter case than in the former. The power factor also cannot be neglected, which would be different in different cases.

An effort to determine the power factor experimentally by placing in the circuit a condenser of known capacity and measuring the partial voltages across the terminals of the ozonizer, and of the condenser, and also the total voltage in the circuit, although giving

fairly good results for very small air spaces failed to give correct values when the air-space was increased. It was found later[1] that in such cases the discharge is oscillatory, and more or less irregular. There is also considerable rectification of the current which was tested by means of a D.C. galvanometer in series.

For this reason the power consumed in the ozonizer was determined by deducting the transformer losses from the readings of a wattmeter placed in the primary circuit of the transformer.

In Table IX. some readings are given to compare the efficiency of such ozonizers as are described in this paper. Readings were taken for one pair of electrodes with two different thicknesses (.05 mm. and .20 mm.) of mica between and also ten pairs of rectangular electrodes mounted on glass, with mica plates .05 mm. in thickness and an air space of .5 mm. between each pair. The readings show an increase in efficiency with increased capacity.

In the table V is the difference of potential in volts, i the current in amperes, W the product of V and i, W' the power consumed in the ozonizer in watts, O the mass of ozone produced per minute in grams and E the yield of ozone per kilowatt hour in grams.

TABLE IX.

Air space between plates 1 mm. Gas velocity .95 liter per minute. Thickness of mica plate .05 mm.

V	$i \times 10^6$	W	W'	$O \times 10^6$	E
3,350	955	3.20	.85	957	67.5
3,550	1,200	4.25	1.2	1,490	74.5
3,700	1,500	5.54	1.8	1,950	65.0
4,030	2,200	8.87	3.0	2,770	55.4
Thickness of mica .20 mm.					
4,470	630	2.81	1.0	990	59.4
4,700	806	3.7	1.3	1,090	50.3
4,900	896	4.4	1.5	1,220	48.7
Ten rectangular plates. Air space between plates .5 mm. Gas velocity 2.85 liters per minute.					
1,620	1,435	2.32	1.0	1,667	100.0
1,650	1,790	2.96	1.4	2,058	88.2
1,700	2,270	3.86	2.0	2,820	84.6
1,730	2,540	4.36	2.5	3,341	80.2

[1]See the writer's article "The Formation of Ozone by Silent Discharge," above p. 117, Fig. 2.

The results of this investigation may be summarized as follows:

1. In all cases studied by the writer the quantity of ozone produced in a given ozonizer was found to be, over quite a large range, almost directly proportional to the current, *after a full steady discharge is established*, and practically independent of the voltage. The phenomenon cannot be explained by the increased ozone density or by the deozonizing effect of the current, as these were varied in many different ways and yet the law seems to hold good in general.

2. A given current passing through a given volume of air does not produce the same amount of ozone in different ozonizers. Other things remaining the same the yield per coulomb increases with decrease of capacity.

3. The efficiency of the ozonizers such as described in this paper was found to increase with increase in capacity.

4. No definite voltage seems to be necessary for the transformation of oxygen into ozone.[1]

DISCUSSION.

Warburg has advanced the theory[2] that the formation of ozone is a photochemical reaction, being due to the action of ultra-violet and cathodic rays on oxygen. In a later article by him and G. Leithauser[3] the author adds that the rapidly moving electrons may have the same effect on the gas as rays of small wave-length.

Although certain elementary substances are converted into their allotropic modifications by the action of light, such transformations are found to take place with *evolution* of heat as, for example, in the transformation of yellow into red phosphorus, or of monoclinic into rhombic sulphur,, giving rise to more stable forms. But as the formation of ozone is accompanied by an *absorption* of energy it is clear that it cannot be classified under the changes of this kind.

A molecule of ozone is found to consist of three atoms of oxygen. Its formation from molecular oxygen necessitates the dissociation of these molecules into their atoms, from which groups of three atoms may be formed. It does not seem probable that such dis-

[1]By suitable arrangement it was possible to produce ozone at 800 volts, and probably this value can be brought down still lower.

[2]Preuss. Akad. Wiss. Sitz. Ber., 46, p. 1011, Nov., 1903.

[3]Ann. der Phys., 20, pp. 751–758, 1906.

sociation can be brought about to any great extent by the *direct* action of ultra-violet light, on the gas. J. J. Thomson has found[1] that ionization produced in air by ultra-violet light is very small. and E. Bloch,[2] repeating Lenard's experiments, came to the conclusion that the ionization reported by him was produced by the light waves striking solid particles in suspension, since when the gas was carefully filtered through cotton wool no appreciable ionization was produced in it. Therefore it appears from these facts that the dissociation is produced by the ions or electrons carrying the discharge which break up the molecules of oxygen into their atoms, rearrangement of these atoms in groups of three giving rise to ozone.

Most of the results obtained during this investigation can be explained on this hypothesis. It has been shown that the amount of ozone produced by a given current through a given volume of air is not, in general, a function of the *current* alone, but also of the *voltage*, within certain limits. Since the velocity of the ions is determined, when everything else remains constant, by the strength of the field in the air space, the greater this force the greater the velocity, and hence the number of dissociations produced by each ion passing through the gas. In other words, assuming a constant source of ionization the current passing through the gas would be proportional to the average velocity of the ions, whereas the kinetic energy of each moving ion would be proportional to the square of this velocity. And if this energy is absorbed by the gas in producing dissociations in it, we would expect to find an increase in the amount of ozone produced per coulomb with the higher voltage.

This relation, however, would not hold indefinitely, since if the air space is small the ions may acquire such a velocity that only a fraction of their kinetic energy will be absorbed in producing dissociations, the remaining part being transformed into heat or other forms of radiant energy at the surface of the opposite plate.

The curves given in Fig. 5, where the mass of ozone per coulomb is plotted with the voltage, confirm this view. In each case the curves show a more or less rapid rise with the voltage at the start but soon approach a constant value. The voltage at which this

[1]Camb. Phil. Soc. Proc., p. 417, 1908.
[2]Comptes Rendus, 147, p. 892, 1908.

critical point is reached is seen to be different in different cases being smaller where the air space is smaller, and probably represents the conditions at which a full steady discharge is established.

It was also found that the efficiency of ozonizers increased with increase of capacity.[1] On examining the oscillographic curves of the discharge current[2] it will be seen that when the capacity is small the curves show an oscillatory discharge like a spark discharge of very large period. As the capacity is increased the curves become smoother and more regular. It is well known that sparks produce little ozone and decompose rapidly what is formed. Therefore it would be natural to expect a higher efficiency with smoother discharges.

In concluding this paper the writer wishes to acknowledge his indebtedness to Professor A. W. Goodspeed for kindly placing at his disposal all the facilities of the Randal Morgan Laboratory of Physics and to Dr. R. H. Hough for many valuable suggestions and criticisms during the course of this investigation.

RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA,
NOV. 18, 1909.

[1]This agrees with the experimental results, and also with those of Ewell's investigation who recommends a thin sheet of insulator of high dielectric strength between the plates and also a small air space, for greater efficiency, both of which would give an increased capacity.

[2]See the writer's article, "Some Observations on the Silent Discharge," p. 117.

THE THERMOELEMENT AS A PRECISION THERMOMETER.

By Walter P. White.

IN electrical temperature measurement the thermoelectric or the resistance method each has advantages of its own which in general are sufficiently familiar. But as applied to precision work at ordinary temperatures—to replace the calorimetric mercury thermometer, for instance—the thermoelectric method has not been as much used, and its advantages are not so well recognized. The present paper aims to throw some light on these, treating especially the construction, accuracy and convenience of the copper-constantan thermoelement. The data were derived from the study of four multiple thermoelements which have been used for about three years as calorimetric thermometers at the geophysical laboratory, and also from the calibration described in the following paper, where two of them were used side by side with a resistance thermometer to measure the same temperatures.

Constantan and copper were chosen as forming, on the whole, the best available combination for work at ordinary temperatures. Constantan and steel, its only serious rival at present, excels only in a slightly higher electromotive force[1] and has the disadvantages (1) steel wire is not so readily obtainable insulated as the others, and (2) with constantan and steel we have two metals instead of one which may cause appreciable error from inhomogeneity—a defect which for most purposes evidently more than offsets the slight advantage in electromotive force.

I. What is the Most Important Part of a Thermoelement?

The significance of much that follows will be clearer in the light of a general theorem regarding thermoelements.

It is now well understood that the one great source of error in

[1]In a special case, W. Jaeger and H. Diesselhorst found copper undesirable on account of its mechanical weakness (Wiss. Abhand. d. Phys.-Tech. Reichsanstalt, Vol. 3, p. 302).

thermoelements is inhomogeneity, which can be diminished by care, first in selecting the material, then in protecting it while in use. In this way, it is possible with the best *new* platinum thermoelements to reduce the error below .02 per cent., and with fair samples of constantan wire below .05 per cent. In the case of constantan, this degree of accuracy cannot be taken for granted without first testing the wire. By combining two or more tested wires so that opposite variations of electromotive force due to inhomogeneity neutralize each other, the error in constantan can be decreased three to ten times, while the increased electromotive force from the multiplication of junctions in series is usually an additional advantage in itself.[1]

For still greater accuracy with constantan elements, and for nearly all work with platinum thermoelements at high temperatures, where contamination can seldom be wholly avoided, the thermoelement must be considered as containing inhomogeneities whose effect must be minimized. The general method of doing this was pointed out in 1900 by Holborn and Day[2] and consists in keeping the temperature distribution constant along the whole thermoelement. This is of course a condition which usually obtains in calorimetric work without the necessity of any special precaution.

A further and great gain can often by secured by paying attention to certain specially important parts of the circuit. This is the method now to be considered.

An inhomogeneous thermoelement is often most easily treated as composed of homogeneous ones connected in series. Thus we may suppose (for purposes of demonstration only) the inhomogeneous circuit to be interrupted by the insertion of numerous short pieces, all of the same metal, so short that the temperature variation through each one is negligible, and so near together that each intervening section of the circuit can be treated as homogeneous. Then if H is thermoelectric power[3] against the inserted metal, and ϑ is

[1] If that is undesirable, a pair of wires can be brought to a common junction at each end, so as to behave like a single wire of greater resultant homogeneity.

[2] L. Holborn and Arthur L. Day, Am. Jour. Sci. (4), 8, 202, 1900, or Drud. Ann., 2, 540, 1900.

[3] In the literature a difference of usage exists as to what constitutes positive thermoelectric power, some writers calling that member of a thermoelectric pair positive

temperature, each section will contribute an E.M.F., E, equal to $H\delta\vartheta$; while for the whole circuit

$$E = \Sigma H\delta\vartheta \quad \text{or} \quad E = \int H d\vartheta.^{1}$$

This is equivalent to the earlier formula,

$$E = \int \theta dH^{2}$$

if taken over the whole circuit, but is, in general, more convenient to use.

It gives at once our general theorem, which is: *Each portion of a thermoelement affects the reading in proportion to the steepness of the temperature gradient in which it lies.* Ordinarily, the temperature distribution along a thermoelement includes several regions of nearly uniform temperature (in baths or furnace cavities) and one, or more often two, regions wherein most of the temperature drop occurs, which may therefore conveniently be called the *temperature gradient regions* (surface of the bath—throat of the furnace). In such cases the *temperature gradient portion* of the thermoelement is of preponderating importance, and in two ways especially:

1. The temperature of the junction is measured by the thermoelectric power, not so much of the portions near to it as of the (possibly distant) gradient portions. This may be made a little clearer by a simple illustration.

into which the current passes at the hot junction, while others call it negative. The confusion which often results, while not serious, is altogether unnecessary, and it seems desirable that those entrusted with the preparation of tables, or some authoritative body, should adopt a uniform usage one way or the other. If the metal into which the current passes at the hot junction is called positive, the thermoelement becomes analogous to a battery and the positive wire has the positive lead from the ice bath, which is, on the whole, the most convenient arrangement in practice. This appears also to have been the original usage. The only conspicuous instance of the opposite usage appears to be in the work of Jaeger and Diesselhorst, which however, on account of its great importance, has had a considerable influence upon the literature; but Prof. Jaeger informs me (informal communication) that the change made in their work was largely accidental, and he is of the opinion that the other usage is on the whole preferable.

[1]Since $\int d\vartheta$ alone is zero for the whole circuit, a constant added to H is without effect on the final result, so that it makes no difference what reference metal is chosen in assigning the value of H.

[2]Constancy of Thermoelements, W. P. White, PHYS. REV., XXIII., 449–474, 1906.

Suppose a simple thermoelement presenting but one departure from homogeneity. Let the thermoelectric power between the two wires be uniform and equal to H_g up to and through the gradient region, as far as a temperature, ϑ_g; from there to the junction let the thermoelectric power be $H_j = H_g + \delta H$, and let the temperature of the junction, ϑ_j, equal $\vartheta_g + \delta\vartheta$.

Then the total E.M.F. is, by formula,

$$H_g\vartheta_g + H_j\delta\vartheta = (H_j - \delta H)(\vartheta_j - \delta\vartheta) + H_j\delta\vartheta$$
$$= H_j\vartheta_j - \vartheta_j\delta H + \delta\vartheta\delta H,$$

and this may be expressed as either $H_j\vartheta_j - \vartheta_g\delta H$ or $H_g\vartheta_j + \delta\vartheta\delta H$. On comparing the last two expressions it is at once clear that the actual reading is very close to $H_g\vartheta_j$, and much nearer to it than to $H_j\vartheta_j$. That is, the reading depends on the *temperature* of the junction, but on the *thermoelectric power* of the gradient portion. The necessary condition for this, that $\delta\vartheta$ shall be small, is of course given in taking ϑ_g outside the gradient region.

2. The constancy of the thermoelement is also largely dependent on the gradient portion. This follows immediately from the preceding for the case of a change in any part of the wire itself. But in case of a change in the distribution of temperature along the wire (such as would come, for instance, from a variation of the depth of immersion in a bath), the effect is the same as if the temperature had remained constant and the properties of the wire had shifted. And this effect will tend to be greatest where the temperature gradients are steepest. Homogeneity is therefore most important in the gradient region.

The gradient portions, then, determine the strength of the thermoelement, and their constancy and homogeneity determine its constancy. They are thus the vital portions of the thermoelement.

Several important conclusions follow:

1. Since the accuracy and constancy of the thermoelement depend largely on the portions lying in the gradient region, attention may be largely concentrated on them, almost to the neglect of the others, in which the homogeneity may be relatively low. To procure and maintain good thermoelements is thus not so difficult as has often been thought.

2. Every time an inhomogeneous element is immersed to a different depth in a bath or furnace, thereby bringing in a new temperature gradient portion, a new element is really brought into play. On the other hand, *a very considerable alteration in the quality of the wire near the junction produces comparatively little effect.*

3. The change in reading observed in cutting off the junction of a platinum thermoelement is generally due not to the loss of the junction but to the resulting lowering of the old gradient portion in the furnace. In amputating platinum elements to restore their value, it is sufficient to bring fresh wire down into the gradient region; the whole contaminated portion need not be sacrificed.

4. The thermoelement thus has the advantage that the portion which needs to be treated carefully and preserved from mechanical strain (the gradient portion) is removed some distance from the portion (the junction) which it is most desirable to bend, pack in small compass, or bring in contact with foreign material. With the resistance thermometer, on the contrary, one considerable constructional difficulty lies in making the bulb thin enough to give a small lag and in providing at the same time for insulation and freedom from mechanical strains.

5. Of course, the error due to inhomogeneities in that portion of the thermoelement which runs through the air decreases proportionately as the temperature measured increases. Hence in measuring moderate temperatures, the most uncertain temperature gradients may be in the air rather than at the surface of the bath. In that case, of course, the best portion of the thermoelement might preferably also lie in that portion exposed to the air.

6. It has been stated that thermoelements containing metals (such as nickel) which have an inversion point show an irregularity *near* the inversion temperature. It is clear from the present discussion that this irregularity would also be observed in reading all temperatures beyond the inversion temperature, since some part of the gradient region would always be at this temperature. More fully, the phenomena are as follows. (It may be well, before proceeding to state them, to call attention to the fact that in discussing or computing the electromotive force of a thermoelement, the only essential factors are temperature and thermoelectric power.[1] It

[1]Constancy of Thermoelements, p. 451.

makes no difference whether the temperature gradient, measured in centimeters, is long or short, or even whether it is uniform, when once the relation between temperature and thermoelectric power has been taken into account.) (*a*) When equilibrium has been attained. If the junction has not reached the inversion temperature, the entire thermoelectric power is that of the uninverted metal. When this temperature has been passed, part of the gradient portion will be in one state, part in another, and the further the temperature is carried the greater will be the extent of the second modification; hence, beginning with the inversion temperature, the resultant thermoelectric power of the whole element will *gradually* change toward that characteristic of the inverted form. The same is true if part of the thermometer melts. (*b*) If the inversion is sluggish. The condition of the wire will be out of step with the temperature and the readings will depend on the immediate previous history of the gradient portion. With advancing temperature, the electromotive force will lie too near that of the uninverted form, and vice versa. This effect can easily be tested by bringing a source of heat up to a definite position on the wire, first from one direction, then from the other. A double effect is here produced, since each end of the heated portion contributes.[1] A single nickel wire, .85 mm. in diameter, tested in this way, showed no perceptible hysteresis effect of this sort *after it was properly annealed*. But there might be a disturbing effect of a very different character due to the inversion, namely, an increase in the lag, due to the latent heat as the junction passes the inversion temperature.

II. Construction of Thermoelements.

1. *Selection of the Wire.*

In many cases, objection to the thermoelement for precision work will lie in the supposed labor of selecting the wire far more than in any doubt as to the accuracy finally attainable. It therefore seems important to state in how far and by what means this difficulty has been reduced. The fundamental problem is simple enough.[2]

[1]By using many turns of wire, a very delicate and accurate test can easily be made. With 33 turns of constantan wire no hysteresis effect as great as .00001 was found for the interval 20° to 100°.

[2]Cf. Constancy of Thermoelements, pp. 453–454.

Different lengths of wire are to be heated (or cooled); the resulting electromotive force then measures the difference in thermoelectric power between the two ends of the heated portion. There is no advantage in determining the inhomogeneities any closer than to about 10 per cent. of their value. If steam is used as a source of heat, therefore, temperature differences of 5 degrees or under along the wire are negligible. The wire, therefore, may be freely exposed to the air of the room; and the temperature of the heated portion need not be very uniform. Any galvanometer which will answer for work with a thermoelement is more than good enough for testing the wire to make it. The junctions between the constantan wire and the copper leads, however, must be within .01 degree of each other. This condition is easily secured as follows: Two short pieces of the sample that is to be tested are soldered to *fine* copper wires, the two junctions wrapped in paper so as to be close together but insulated, and then protected from temperature change by a kerosene bath or a thick wrapping. The copper leads are then connected to the galvanometer, which has a device for eliminating the effect of the accidental electromotive forces of its own circuit. The wire to be tested is now clamped (not too near the hot portions) to the two short pieces.

For an accuracy not exceeding .05 per cent. (about .01° at ordinary temperatures) wire should be obtainable whose inhomogeneity is negligible.[1] Wire for such use can be tested very rapidly by simply pulling it quickly through a bath of hot kerosene or paraffine. Portions showing excessive inhomogeneity are then merely rejected. If much greater accuracy is desired, the wires will generally have to be paired so as to give a small *resultant* inhomogeneity and the relative thermoelectric power of the different portions must be known. That involves comparing each part of the wire with one fixed portion, and calls for a larger heated inclosure. This presents no difficulty, but the work is greatly facilitated if a little care is taken to arrange for handling the wire without twisting or kinking. Methods for doing this have already been described,[2] but a recent apparatus is more convenient and satisfac-

[1]Compare A. D. Palmer, PHYS. REV., 21, 65, 1905; also footnote, p. 143.

[2]Constancy of Thermoelements, pp. 454–457.

tory. Its essential feature is a relatively large drum on a small shaft, like a wheel-and-axle. The wire is put on so as to unwind from both at once, hence, in unwinding a large amount of wire from the drum, the corresponding portion delivered from the axle is short enough to stow itself comfortably within the apparatus. There is thus no difficulty in keeping a fixed portion at the edge of the bath, whose thermoelectric power is compared with that of all the other portions as they are successively pulled out. The whole is immersed in a bath of melted paraffine (kerosene would also answer) which is heated in a covered water-bath (Fig. 1). In this apparatus the temperature along the heated wire may vary a few degrees. This variation is practically negligible and can easily be avoided, if live steam is used. On the other hand, the newer form handles long pieces of wire with almost no waste, is compact, ready for use at short notice, and is especially convenient if a permanent supply of live steam is not at hand. It can be loaded with ten or more meters of wire and then stands ready to deliver at will wire calibrated according to requirements with the minimum of time and trouble. After calibration, the wire is indelibly marked (as by tying a knot at some point) and the relation of this mark to the calibrated portion very clearly recorded. Experience has shown that it may not be superfluous to mention this simple precaution. The results of calibration are most conveniently shown by plotting. This gives a map of the condition of the whole wire, and selections can then be made of wires with opposite variations in thermoelectric power, or of portions specially uniform to go in the gradient region, or both. From three to six meters can be examined in an hour. This includes a preliminary rapid examination of the whole wire to insure the absence of large short irregularities, and a series of readings at 5-cm. intervals throughout the wire, repeated to insure accuracy. The time taken is thus not at all serious.

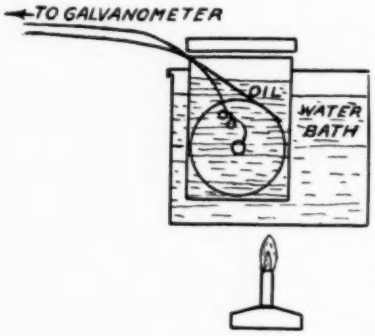

Fig. 1.

Fig. 2 shows the (quite typical) compensation obtained between two constantan wires in a multiple element. The original inhomogeneities are about .1 per cent. of the thermoelectric power of one couple.[1] The resultant inhomogeneity (middle line) is about one eighth of that, but is evidently better still in the gradient portions, G, G'. Hence this pair should give an accuracy exceeding .003 per cent. with a somewhat variable depth of immersion in the bath and better still if the depth is constant—as, in fact, it does.

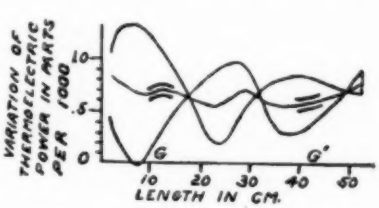

Fig. 2. Showing how two nearly homogeneous wires are combined to give a resultant homogeneity 30 times as great in the gradient portions, G, G'.

2. *Further Details of Construction.*

After the wire is selected, the construction of a thermoelement is of the easiest. But the following points seem worth mention:

1. *Soldering.*—Soldering wax, said to "contain no injurious elements," was found to be essentially a solution of zinc chloride in vaseline or something similar, and earlier thermoelements soldered with it became blackened near the junctions from chemical action. Difficulty was predicted, however, in soldering constantan with rosin alone, but the following method gave in every case a perfect joint on the first trial. The insulation was pushed away and the wires were twisted together with tweezers without touching the fingers; the joint was next dipped in melted rosin, and then, by a quick motion, into a bath of solder.

2. *Inclosure.*—As the simplest and most complete protection from chemical and mechanical injury, these thermoelements have always been completely inclosed in rigid cases.[2] Both glass and sheet metal

[1]Since in making a thermoelement of such wire it is exceedingly improbable that the thermoelectric power of the gradient portion would ever be changed by the maximum difference existing in the whole wire, a single couple made from such wire might safely be counted on for *at least* an accuracy of .05 per cent. (or .02° at 40°) and considerably more with constant depth of immersion.

[2]Although good results have been reported for a flexible inclosure in rubber tubing, that method has appeared rather dangerous, since contact with rubber tarnishes metal, and a layer of tarnish introduces an inhomogeneity into the thermoelement (Constancy of Thermoelements, p. 471). But a good deal can be done to the middle of a thermoelement as long as the gradient portions are completely and rigidly inclosed.

have been used. The process of inclosing in glass is much the easier. Each end of the thermoelement is simply pushed into a suitably bent tube, drawn out thin and fine at the closed end where the junctions are; the two tubes come together at the middle of the thermoelement, and are joined together there by means of sealing wax and an overlapping sheath of brass.[1] The leads come out through the sealing wax. The metal cases were made by bending sheet metal around the thermoelement. Thin brass 0.1 mm. in thickness was used, which, on account of its lower thermal conductivity, is much better than copper. The main object in trying metal cases was to diminish the time lag, but the lag was found to depend more on the insulation than on the material of the case.[2] The operation of inclosing the elements in metal, though simple enough, took more time than all the rest of the construction put together; moreover, it is hard to be certain that the soldered joint will not develop a leak. Hence the simpler and quicker method of enclosing in glass seems generally preferable.[3]

3. *Insulation.*—The original silk insulation was of course removed for a few millimeters near the junction, and had to be replaced. The substitute should not be too thick, as this would necessitate a large and clumsy inclosing tube. Of various things tried, two can be recommended: (*a*) To wind both bare wires together with silk floss till they are covered; (*b*) or, preferably, for elements of numerous junctions, to use some tough lacquer which is not much attacked by paraffin at 100°. Cellulose acetate, soluble in chloroform with 8 per cent. of wood alcohol, is excellent. It behaves like collodion

[1]A preferable arrangement in many cases would appear to be a purely mechanical fastening, with the joint sealed, say, by paraffin, which would allow the glass tubes to be readily changed, and the form of the whole thermoelement thus easily altered.

[2]The lag of calorimetric thermometers is really far less important than was for a time supposed (PHYS. REV., 27, 526, 1908); again, the lag of any electric thermometer includes that of the galvanometer, often two seconds or more; hence the importance of an infinitesimal lag in the *bulb* of such a thermometer may easily be overestimated.

[3]H. Kammerlingh-Onnes and C. A. Crommelin (Versl. K. Ak. van Wet, 12, 625, 1903) found the vertical conductivity of a metal inclosure too great and developed an ingenious combination of glass tube and metal tip. Since an immersion of 6 cm. was sufficient to avoid all difficulty from vertical conduction in the present case, and since a jacket of poorer conducting German silver would give results better still, it would seem that for most purposes a properly constructed metal jacket should be satisfactory wherever the simple glass tube alone would not do.

and is a fine insulator. Shellac, also, would probably prove satisfactory.

4. *The Calorimetric Thermoelements.*—The thermoelements studied, four in number, were all of four couples each. They give 160 microvolts per degree. Really, they constitute only two thermoelements, each one divided in two for convenience in testing, but commonly used entire. The smallest electromotive force read, .1 microvolt, therefore corresponds to .0003°.

The first pair, *A* and *B*, were 50 cm. long, and were of wire .12 mm. in diameter (no. 36) giving about 70 ohms resistance each. In the others, *D* and *E*, the constantan wire was of twice the diameter (this was the wire described on page 143), and the resistance about 20 ohms each. The difficulty of adjusting the galvanometer circuit was thus reduced as well as the danger of error from imperfect insulation. The *thermal* conductivity of the constantan still is less than that of the no. 35 copper wire, so that the conductivity of the whole thermoelement is not greatly increased by the change. Probably still larger wire, say .3 to .4 mm. in diameter, would often be better still.

III. Determining the Temperature from the Thermoelement Reading.

The calibration curve of the copper constantan thermoelement is treated in the following paper, but the special working table used to reduce microvolts to degrees has proved so convenient that a description of it also seems worth giving.

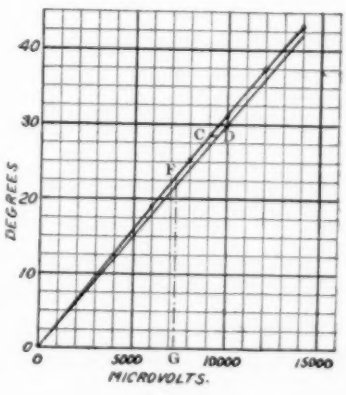

Fig. 3.

At first the values of the temperature, ϑ, were tabulated as functions of the electromotive force at intervals of 10 microvolts. Since readings were made to .1 microvolt, the interpolation interval covered 100 units and the process of taking a temperature from the table then

involved copying a number of figures, computing the interpolated value by a slide rule, and adding. The defect in this arrangement was of course that no advantage whatever was taken of the nearly linear relation between microvolts and degrees. Accordingly, a series of numbers was tabulated which when added to the microvolts gave numbers proportional to temperature and equal to it on multiplication by .003. The variation in these correction numbers runs from 0 to .5 microvolt, for the 10-microvolt interval, and the interpolation can therefore be done at sight. The significance of this method may be made clearer by Fig. 3, where *CD* represents the correction function, evidently varying much more slowly than the temperature, *FG*. The multiplication by 3 can generally, in actual work, either be done once for all at the end of a series of operations in which "corrected microvolts" are handled, or else avoided altogether by a change in one of the constants entering into the operation.

A great disadvantage of the electrical thermometer has recently been said to lie in the laborious computations required with it. The complete calculation of one ordinary calorimetric determination, for instance, has been said[1] to occupy several hours. This estimate is no doubt justified in the case of some particular apparatus and procedure, but is, in general, excessive. The proof that it is so for the calorimetric part of the calculation belongs, of course, in another place. As far as the present thermoelements are concerned, the temperature computations required for a calorimetric determination are two in number and take on the average forty seconds.

IV. ACCURACY.

One great advantage of thermoelements is the ease with which they can be tested comparatively by connecting two in opposition. The effect of changes in the bath temperature then becomes largely negligible[2] as well as the errors of the auxiliary apparatus. The ice tank can usually be replaced by a bath at room temperature with a gain in both convenience and accuracy.

[1]By T. W. Richards and R. H. Jesse, Jour. Am. Chem. Soc., 32, 269, 1910.

[2]Save when the lag of the two is different—a point which may give trouble if overlooked.

1. *A Uniform Temperature Bath.*

For the direct comparisons, the simple bath shown in Fig. 4 proved very effective. In this the irregularities in temperature due to the loss of heat from the surface were minimized: (1) By winding the electric heating coil uniformly and quite near the sides of the vessel, so that it and the outside surface merely neutralized each other's effects; (2) by having an upper chamber, separated by a partition and maintained at the same temperature as the lower. (3) The loss of heat from the bottom was expected (and found) to produce no trouble. The bath was used immersed in a pail of cotton wool. The stirrer was in a vertical central tube, into which the thermoelements dipped. The partition between the upper and lower chambers should fit as tight as possible, but a single hole large enough to allow the thermoelements some freedom of motion was found to be harmless if no other opening was permitted. Equality of temperature between the upper and lower chambers was secured by shunting one of the heating coils in accordance with the readings of a differential copper constantan thermoelement permanently fastened in place. The temperature regulation proved surprisingly easy.

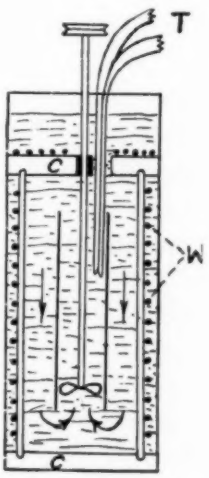

Fig. 4. Two-chambered bath for uniform [and constant] temperatures. *C*, *C*, [cork] partitions; *W*, [wires of] heating coil; *T*, thermoelements.

This apparatus was made of a tin can, 10 × 25 cm., two large corks just fitting it, and six sticks of dowel. The corks and dowel formed a frame on which the heating coil was wound and the upper cork served as a partition between the two chambers. The upper heating coil was laid flat on its surface. Kerosene was used as the bath fluid for the following reasons: (1) The insulation of the heating coil did not have to be water-proof; (2) bare thermoelements could be handled when desired; (3) there was less evaporation than with water, and higher temperatures could be reached; (4) whatever vapor was produced tended in condensing to improve and not prevent insulation. In the neighborhood of 100° thermoelements

could be moved up and down 2 cm. in this bath without detecting a difference of .001° in temperature.

2. *Results of Comparative Tests of the Thermoelements Alone.*

1. *Lag.*—The lag was measured by direct comparison in the kerosene bath with an element having its wires bare, whose lag was taken as 0. Further intercomparisons indicated that the results were correct to about 2 per cent. Two metal inclosed elements with mica insulation gave about .9 second; one with paraffined paper insulation 1.7 seconds, which was nearly as great as that obtained for glass inclosure (2 seconds) by a less accurate method. (Paraffined paper proved unreliable as an insulator in one instance and is not recommended.)

2. *Uniformity of the Temperature Gradient Portions.*—The most important characteristic, the uniformity of the temperature gradient portions, was tested in various ways, of which the most delicate, with *B*, *D* and *E*,[1] was obtained by moving each up and down 2 cm. with the bath at 90°. The variation in reading was imperceptible —that is, it was less than .001 per cent. Tests through a greater distance, but with somewhat less delicacy, gave the same negative result. Hence with these thermoelements even a constant depth of immersion was not necessary to obtain an accuracy of .001 per cent. up to 90°, which corresponds to an accuracy of .0003° near room temperature. With constant immersion the accuracy is of course considerably higher.

3. *Relation of the Ends.*—Even if both gradient portions of a thermoelement are perfect, yet if they differ from each other in thermoelectric power the reading will depend upon the room temperature. This difference can be measured by reversing one thermoelement of a pair. It ranged from .0001 to .00003 for the same three thermoelements. These thermoelements will therefore show at all temperatures a roughly calculable variation of from .001° to .0003° for 10° variation in room temperature.

The above results indicate that, as far as the effect of inhomogeneity is concerned, an accuracy of .0001° could generally be obtainable with certainty under such uniform external conditions as would generally prevail where this high accuracy is desirable. Of

[1] *A* was spoiled (during inclosure in metal) before these tests were made.

the other causes of error residing in the thermoelement itself, defective insulation[1] and mechanical strain are preventable, and the parasitic E.M.F.'s in the copper leads can be made negligible.[2] Any change or error can easily be detected at any time, and at any temperature, whether very constant or not, simply by connecting the two halves of the thermoelement in opposition. It is on this account that the thermoelements were each made in two sections. After the preliminary tests two such sections may as well be inclosed in a single case, if that seems more convenient.

3. *The Accuracy as Limited by the Auxiliary Apparatus.*

A potentiometer reading of a thermoelement is a comparison of its E.M.F. with that of a standard cell, accomplished by means of resistance coils and of a constant comparison current, whose potential drop along different resistances is made to balance successively the various E.M.F.'s.

1. In the *absolute* measurement of temperature the largest errors will ordinarily come from the imperfect adjustment of the coils, or their variation from day to day. For instance, coils accurate to .005 per cent. would give temperature readings good only to .001° at 20°. This exceeds the present accuracy of the standard temperature scale, it is true, but does not call for a precision of .0001° in reading.

2. The need for reading to .0001° arises in the measurement of small temperature variations, such as it is often desirable to use in calorimetry. A temperature interval of 1° (for instance) can thus be measured to .01 per cent. This requires only a corresponding accuracy in the coils used to balance the temperature variation, which therefore, cease to be the main source of error. But it does require that those parts of the system whose values vary in pro-

[1]The insulation resistance between the thermoelements *D* and *E* and the metal case is indefinitely more than 60 megohms.

[2]Random samples of commercial wire and sheet copper gave a maximum difference in thermoelectric power of only .006 microvolt per degree; a thorough attempt to harden the wire caused an increase of only .02 microvolt per degree. Moreover, all contact E.M.F.'s in the copper leads naturally will and always may enter as oppositely directed pairs. It is only for the most delicate measurements that these E.M.F.'s need receive any attention at all. A necessary requirement, however, for absence of parasitic E.M.F.'s is that all contacts shall be good. See Phys. Zeitschr., 8, 327–328, 1907; also PHYS. REV., 30, 784, 1910.

portion to the temperature reading as a whole shall have (for the time of the experiment only) a constancy corresponding to .0001°—that is (for instance), equal to .000,004 for readings near 25°.

(*a*) A Weston (unsaturated) standard cell more than fulfils this requirement. Even a saturated cadmium cell can readily be made to do so. It is easily shielded from rapid changes of temperature, and needs to be kept constant only to .1°.[1]

(*b*) The total temperature reading varies also with the *ratio* of the two potentiometer resistances used to balance, first the standard cell, and then the measured E.M.F. The variation here can arise only through the difference in the temperature coefficients of the two. This difference may reach over .000,040, and is likely to be .000,010, per degree;[2] the latter value would require that the temperature of the coils be constant to .3° in reading to .0001°. Of course, a direct test would be necessary to show that greater constancy was not required. With some apparatus attention would need to be given to controlling or observing the temperature of the coils.

(*c*) The comparison current is adjusted frequently in accurate work, hence its variations, if not excessive, are an inconvenience rather than a source of error. With a storage cell directly exposed to the temperature changes of an ordinary room, the inconvenience may be appreciable, but a shielded cell was found seldom to vary .000,002 in ten minutes in a room of very variable temperature. The shielding was done by putting the cell within (but not touching) a larger body of water (20 liters) and then surrounding this with sawdust heat-insulating packing. It is easy to show that the combination of a heat absorber with a heat insulator is usually more effective than either alone.

Continuous observations of the above cell for periods of 30 minutes or so have never shown any *sudden* fluctuations as great as .000,001. Trouble of this sort apparently is due to defective cells and is avoidable. Hulett[3] has also used a very large cadmium

[1] Its temperature coefficient being only .000,040 per degree.

[2] E. B. Rosa, Bull. Bur. Standards, 5, 419, 1909.

[3] G. A. Hulett, PHYS. REV., 27, 33, 1908.

cell as the comparison cell in a potentiometer, with an even greater increase in steadiness.[1]

Of course, the comparison current must not be interrupted during the time taken for the zero adjustment,[2] but must then pass through a substitute resistance.

(*d*) The constancy of the ice-bath also affects the thermoelectric temperature reading. For absolute measurements this effect is the same for the resistance- and mercury-thermometers, since these, too, use the ice point as a point of reference. But in relative readings of small temperature differences, these other thermometers do not need such a point, while with the thermoelement every reading is a comparison of another temperature with that of the bath. Hence if the bath varies appreciably within an hour or so, the accuracy of the thermoelement is (to that extent) impaired. But observations with the very sensitive resistance thermometers of the Bureau of Standards[3] have shown their ice-baths constant for hours nearly or quite to .0001° as long as the thermometers are not moved. Several direct comparisons (by thermoelements *D* and *E*) of two baths made with commercial ice showed both constant for hours to within the error of reading, which was about .00015°.[4] The variation of a good ice-bath is thus at any rate less than .0001° for the time of an ordinary calorimetric determination.

4. *Differential Measurements.*

The thermoelement in itself can only compare temperatures; hence the necessity of introducing an ice-bath to give a temperature of reference in ordinary measurements. If the required measure-

[1]There are also other possibilities with the storage cell. With a sufficiently dilute electrolyte such a cell has a zero coefficient (its use was suggested by Dr. J. K. Clement); the durability, etc., of such a cell does not seem to have been tested. Again, a moderately low resistance of copper, placed close to the cell, and in series with it, can be made to largely compensate the variations in E.M.F. due to temperature.

[2]The adjustment described in, for instance, Potentiometer Installation, PHYS. REV., 25, 344, 1907.

[3]Informal communication.

[4]This strongly indicates that the variations often found in the ice point of resistance thermometers (see, *e. g.*, Bull. Bur. Standards, 3, p. 648, 1907) are not due to the bath, but to some effect in the thermometer, perhaps to mechanical strains. Later — This view has now been confirmed by the construction of resistance thermometers for which the variations are much smaller. (Informal communication.)

ment is differential in the first place, this necessity disappears, and the elimination of the bath brings with it the further advantage that the maximum temperature difference present need now be no greater than the interval measured; this diminishes greatly the errors both from temperature change in the auxiliary apparatus and from inhomogeneity in the thermoelement itself. The proportionate accuracy of the resistance coils can thus be made available for intervals almost indefinitely small.

The same advantage can also be secured for the direct reading of temperature *changes* (as in calorimetry) by substituting for the ice-bath a suitable comparison body, which may be a block of metal, jacketed like the best calorimeters. The slight changes in such a body can be allowed for by a cooling correction smaller and more accurate than that of the calorimeter, or can be eliminated by a thermostat in the jacket. Hence such a body introduces practically no error, while it eliminates several, and is as convenient as an ice-bath. A further discussion of this method is in preparation.

5. *Sensitiveness.*

Moving coil galvanometers are regularly on the market whose coils have a moment of inertia of .25 c.g.s. unit.[1] Such a coil, used with a period of 5 seconds and with a resistance of 200 ohms in circuit, will give a deflection of a millimeter per microvolt at a meter's distance.[2] If the smallest quantity readable be taken (as usual) equal to the tenth of a scale division, this would then, for thermoelements *D* and *E*, correspond to .0003° at 1 meter or .0001° at 3 meters scale distance. Some moving coil galvanometers will do twice as well, and a still greater sensitiveness can be reached with a fixed coil galvanometer. It is also easy, however, to increase the original sensitiveness of the thermoelement itself two or three times by increasing the number of couples in it. This seems decidedly preferable, for it diminishes the annoyance from parasitic E.M.F.'s, at the same time that it renders a precision of .0001° in reading easily attainable with a very convenient type of galvanometer. The sensitiveness of the thermoelement is therefore more than suf-

[1]The galvanometer coil now used with the elements *D* and *E* has a moment of inertia of only.16 unit, yet is large enough to carry a very fine mirror 12 mm. square.

[2]Every-day Problems of the Moving Coil Galvanometer, PHYS. REV., 23, 382, 1906.

ficient for the accuracy otherwise attainable in direct reading. In the differential use of the multiple thermoelement, on the contrary, the limit to accuracy will generally be set by the sensitiveness.

A multiple thermoelement of twenty couples, then, can easily be constructed, and, with proper auxiliary apparatus, will give results *relatively* accurate (save for possible calibration errors) to .0001° for small temperature intervals. This is not an extreme limit, but the value which should be attainable with a practical and convenient installation. The *absolute* accuracy is essentially that of the resistance coils used.

V. Field of the Multiple Thermoelement.

The real value of the multiple thermoelement of course depends not on its accuracy alone but on how it compares in this and other respects with other forms of precision thermometer. With respect to the mercury thermometer its advantages and disadvantages are largely those of electrical thermometers in general, hence the question reduces itself to a comparison with the resistance thermometer.

In this comparison the value of the multiple thermoelement will rest on other advantages than those which are more familiarly associated with the simple thermocouple. Adaptability of form and wide range are precluded by the inclosure and the silk insulation. The great indifference of the thermoelement to mechanical strain, however, is especially important in view of the compactness often desirable in calorimetric thermometers. Aside from it, the balance of advantage will generally depend on the auxiliary apparatus. Here a fairly definite comparison is possible, since the respective electrical installations have an essential resemblance. In each the thermometer is balanced against a standard (an electromotive force in one case, a resistance in the other) by means of auxiliary resistances, a galvanometer, and an auxiliary battery.[1]

The possible sources of error with the thermoelement have been found to lie in: (1) Errors in the resistance coils. These affect the *absolute* accuracy proportionately. They affect both instruments to the same extent. The other sources of error practically

[1]The potentiometer method as used with the resistance thermometer is of inferior accuracy, and is not considered here.

affect only the *relative* accuracy. They are: (2) Change in the standard of comparison; (3) change in the ratio of certain resistances; (4) change in the comparison current; (5) change in the ice-bath; (6) parasitic thermal E.M.F.'s; (7) lack of sensitiveness; (8) inhomogeneity. (2, 3) With the resistance thermometer, the temperature measured is proportional only to a small increment of the electrical quantity measured, and a change in the standard or in the ratio coils causes ordinarily ten times as great an error as with the thermoelement. With manganin of average quality, therefore, the standard coils of the resistance thermometer may often need to be constant nearly to .03° for an accuracy of .0001°, and in general an accuracy even as low as to .001° cannot be much exceeded without some means of regulating the temperature of the auxiliary coils. (4, 5) These cause no error with the resistance thermometer, and are sources of inconvenience rather than error with the thermoelement.[1] (6) These also may be considered sources of inconvenience rather than of error. Their effect is inversely proportional to the E.M.F. (per degree) at the galvanometer terminals. This E.M.F. is 320 microvolts for $D + E$ and could readily be made at least 800 microvolts. The largest value of it for any resistance thermometer of which I have been able to learn is 520 microvolts.[2] (7) The sensitiveness (taking as usual, that of the galvanometer

[1]The ice-bath must be fairly near the hot junction. In some cases this requirement would be troublesome, or even prohibitive, but usually the ice-bath merely adds to the day's work ten minutes or so of extra manipulation, none of which comes during observations.

A standard cell observation requires but ten or fifteen seconds; moreover, it is a stationary reading; it also demands a relatively low sensitiveness, and hence adds no accidental error. In this respect it is less objectionable than the observations with reversed ratio coils which are often necessary with the resistance thermometer. The experimental arrangements needed for the storage cell may be offset by those needed to avoid contact resistance errors in the resistance thermometer system. Hitherto, the prevention of such errors has demanded either computation-compelling shunts or undesirable mercury contacts.

[2]Informal communication from the Bureau of Standards. This thermometer was heated only .002° by the comparison current. The E.M.F.'s in the thermoelement leads beyond the zero adjusting switch (Potentiometer Installation, p. 344) are not fairly included in this comparison, but should be charged to inhomogeneity of a part of the thermoelement. They may easily be made entirely negligible. So, also, may the E.M.F.'s in that switch, except for work far transcending in delicacy and difficulty anything considered here. On the construction of neutral switches, see PHYS. REV., 30, 784. 1910.

proportional to $1/\sqrt{R}$, where R = total resistance) is proportional[1] to the terminal voltage $\div \sqrt{R}$, and will therefore have among different existing instruments about the same relation as the terminal voltage itself. Hence the thermoelement is easily quite as sensitive as any resistance thermometer yet reported. The resistance thermometer, however, seems to have a greater possible sensitiveness,[2] and may prove useful in measurements even more delicate than any yet attempted. But very high sensitiveness has its drawbacks,[3] and though sometimes useful in technical apparatus, does not yet appear to have been found of practical advantage in precision work. (8) The possible errors from inhomogeneity may be set against those from mechanical strains in the resistance thermometer.[4] Both doubtless can be, and probably already have been, made negligible for calorimetric measurements.

The thermoelement, therefore, is as sensitive and as accurate as the resistance thermometer has yet been made. The real balance of advantage between them hence reduces itself to questions of convenience or adaptability. And these will usually depend chiefly on whether one instrument or several is to be read.

If several different thermometers are successively connected to the same auxiliary system, frequent changes of contact are necessary. High sensitiveness with the resistance thermometer involves very great precision in the measurement of a small resistance, and it would be difficult, to say the least, to prevent this from being affected by the switch contacts, to say nothing of the further complications possibly introduced by compensating leads.[5] The potentiometer, on the contrary, is quite indifferent to small contact resistances in the external circuit.

[1]Cf. W. Jaeger, Ueber die Empfindlichkeit der Widerstandsthermometer, Zeitschr. f. Instr., 26, 279, 1906.

[2]Since for either instrument sensitiveness depends ultimately upon size, and a further great increase in size may present less difficulty with the resistance thermometer.

[3]Cf. W. Jaeger, Empfindlichkeit, etc., pp. 282–284.

[4]See footnote, p. 151. For a very striking illustration of these, see Jaeger and von Steinwehr, Anwendung des Platinthermometers bei kalorimetrischen Messungen, Z. Inst., 26, 242, 1906.

[5]This assumes the use of the bridge as an auxiliary. The differential galvanometer method of Jaeger and von Steinwehr (*loc. cit.*) ("overlapping shunt" method of Kohlrausch) avoids in part this particular difficulty, but has very decided inconveniences of its own.

When several thermometers are in use at once, it will usually happen that some of them may be of low accuracy, or that some should preferably have the same calibration constants. Here an advantage would lie in the ease with which simple thermoelements can be made and intercompared, or duplicated by simply cutting them from the same sample of wire.

If one of the temperatures is above 1000°, or requires a thermoelement for any other reason, it becomes impossible to use the bridge alone and the use of the resistance thermometer compels a duplication of apparatus, and often the addition of another observer.

The potentiometer is a more comprehensive instrument than the bridge, and its advantages are not confined to temperature measurement alone. If measurements of current, voltage, or watts are required, as frequently in calorimetry, these can by its use be readily combined with the temperature measurements. For instance, in calibrating the present calorimeter, it has been possible for one observer to take, within the same minute, accurate readings of the temperature and also of the voltage and of the intensity of the heating current.

All these advantages are still further increased if the potentiometer is one on which several independent switch settings may be made at once, and different voltages thus read alternately without resetting.[1] In fact, a very important advantage of the potentiometer, hitherto but little appreciated, lies in the fact that it can easily be arranged in this way.[2]

The above advantages of the multiple thermoelement are, to a large extent, those of the potentiometer. Where a single instrument is to be read they vanish, and the balance of advantage, depending mainly on the factors considered in footnote 1, p. 146, may often be on the side of the resistance thermometer.

For differential measurements, however, between bodies not too far apart, the thermoelement, as shown above, loses nearly all its disadvantages, and becomes somewhat simpler and more certain in its performance than the resistance thermometer,[3] when used in the

[1]Zeitschr. f. Instr., 27, 218, 1907.

[2]A potentiometer of this kind has proved of great value, and an article on the construction of such is in preparation.

[3]Since this latter is still left with the full possibility of error both from mechanical strain and from temperature change in the ratio coils.

same way. The same advantages can also be obtained in calorimetric and similar work by the use of a comparison body in place of the ice-bath.

Summary.

1. The E.M.F. of a thermoelement, whether homogeneous or not, can be expressed as equal to $\int H d\vartheta$ (H, thermoelectric power, ϑ, temperature). It follows that the effect of each portion of a thermoelement is proportional to the magnitude of the temperature gradient in which it lies; hence the vital parts of a thermoelement are the parts along which the temperature varies; they mainly determine the calibration and the constancy; with them alone need the maker or user of the thermoelement be much concerned. In changing them (as by varying the depth of immersion in a furnace) the thermoelement itself is changed, if not homogeneous, while alterations in regions of uniform temperature distribution, as at the junction, have little effect on the temperature measurement.

2. Commercial constantan wire good enough to make thermoelements accurate to about .05 per cent. is easily obtained and costs but little trouble in the selection, but cannot be relied upon without any test for possible inhomogeneity. Compensated thermoelements of higher accuracy, reading consistently to .0001°, for use at ordinary and low temperatures, can be made in a day or two each. Improvement in the accessory apparatus has shown that their constancy is about ten times that shown three years ago.

3. The accuracy of .0001° reached by the thermoelement can also be attained in its auxiliary apparatus (potentiometer, etc.). The resulting accuracy, both absolute and relative, and the sensitiveness are quite comparable with those of the best resistance thermometers yet used.

4. For the measurement of single temperatures, the resistance thermometer is often more convenient. On account principally of the comprehensiveness of the potentiometer and its indifference to external contact resistances, the thermoelement is usually preferable where several different measurements are to be made at once. The thermoelement is also usually superior for differential measurements, and its advantages in this respect can be made available for calori-

metric work by the substitution of a suitable comparison body for the usual ice bath.

5. A very convenient wire tester, a simple bath for testing and comparing thermoelements, and a convenient form of tabulation for calibration curves are also described.

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WASHINGTON, D. C.,
March 31, 1910.

THE CALIBRATION OF COPPER–CONSTANTAN THERMOELEMENTS.

By W. P. White, H. C. Dickinson and E. F. Mueller.

THE practical usefulness of a thermoelement will often depend on whether its readings can readily be interpreted in terms of the standard scale of temperature, that is, on the ease and accuracy with which it can be calibrated. The present work was undertaken for two reasons, first, to obtain a calibration curve for a particular pair of elements which had been in use at the Geophysical Laboratory, and second, to obtain data relating to the calibration of copper-constantan thermoelements in general.

The two elements in question were compared with two platinum resistance thermometers, which had been very carefully calibrated in terms of the international hydrogen scale.[1] The comparison was made at the Bureau of Standards, the thermoelements and accessory apparatus being brought over from the neighboring Geophysical Laboratory. The thermoelements were the *A* and *B* briefly described in the preceding article. They were read according to the method already published,[2] using two leakage shields and the simple potentiometer there described. The resistance thermometers were used substantially according to the method followed in the original calibration. A water-bath, which is ordinarily used for the testing of clinical thermometers,[3] was utilized for the comparison. During the progress of the work the bridge, the potentiometer and the standard cell were calibrated.

The data for the resistance thermometer were most conveniently worked up in sets of four. The corresponding thermoelement readings were simply averaged. Each observation here given therefore represents the mean of four readings. The resistance thermometers were read to 0°.0001 and the thermoelements to 0°.0003, the

[1]Bull. Bureau of Standards, 3, 641, 1907.

[2]Potentiometer Installation, Phys. Rev., 25, 334, 1907.

[3]Bull. Bureau of Standards, 1, 284, 1904–5.

difference in sensitiveness being practically due to the difference in the galvanometers used. The greater convenience of the partial deflection method[1] as compared with the null method of reading the instruments, especially with a somewhat irregular temperature, became very evident in this work. To facilitate computation, all the readings were taken at temperatures very close to the even degrees, and reduced to even degrees by using a preliminary calibration formula. These reduced results were used in all the subsequent computations, and are the ones which appear in Table I.

The observations were made in two sets, the first taken on July 9 and 10, and the second on July 30 and 31, 1907.

The precision of the readings is indicated by the results of the second set (Table I.), where a storage battery was used for heating to secure a more constant temperature in the bath. The value for 100° was obtained directly from the temperature of steam, which was computed in the usual manner from the barometer reading.

TABLE I.

Second Set of Observations.

Two elements in series. 1 microvolt =0°.003 approximately.		Single element. 1 microvolt =0°.006 approximately.	
Temperature.	**Microvolts.**	**Temperature.**	**Microvolts.**
30°.0000	9,633.7	65°.0000	10,818.8
	9,633.7		10,818.9
35°.0000	11,301.4	75°.0000	12,605.5
	11,301.5		12,605.4
	11,301.4		12,605.2
	11,301.4		12,605.5
40°.0000	12,984.0	82°.0000	13,874.3
	12,983.8		13,874.2
	12,984.1		13,874.5
55°.0000	18,135.4	100°.000	17,222.0
	18,135.4		
	18,135.4		

[1]H. B. Brooks, Bull. Bureau of Standards 2, 228, 1906; Potentiometer Installation, p. 337.

These results include the observational errors of both systems, as well as those due to the irregularities in the temperature of the bath. It will be seen that the differences are, in most cases, no greater than the smallest quantity read with the thermoelements. The results of the first set show a larger average difference (about 0°.001) which was undoubtedly due to the unsteadiness of the bath temperature on those days. The readings at 40° given in Table I. were taken before the bath had been protected by an additional heat-insulating wrapping. Since these and those at higher temperatures are the only ones to show appreciable discrepancy, this may also be attributed to the bath. The uniformity of the calorimetric readings obtained in daily work with either installation is usually better than that shown here.

In spite of the consistency shown by observations extending over a short time, the final accuracy of the calibration, as indicated by the agreement on different days (see Fig. 1), is only about 0°.004, an error too great to be chargeable to the resistance thermometer and equal to twice the probable error of the standard temperature scale. This error seems mainly due to two causes. (1) During the first set of observations, the temporary potentiometer set-up was not quite satisfactory and there was some evidence of leakage at 55° and above, due to condensation upon the leads of steam from the bath. In the second set greater precautions were taken against this source of error, and careful tests indicated its entire absence. (2) Most of the error, however, is due to the bath, whose temperature was found, after the work was done, to be less uniform than had been supposed. In the second set, for instance, when leakage error was entirely absent, there is still a discrepancy between the results of the third and fourth days, which may be an effect due to the extra jacketing of the bath on the fourth day. Of course, errors from such a source do not reflect upon the value of the electrical methods of temperature measurement, but indicate, rather, that considerably greater accuracy could be attained. However, the accuracy already secured is sufficient for the objects of the present investigation.

Formulæ.—As one prime object of the present work was to determine the character of the copper-constantan calibration curve in

general, some study was given to the mathematical representation of the results. Of the numerous formulæ obtained, it seems sufficient to give the following. If the curve

$$E = 155.195\theta + 0.178\theta^2 - 0.0002\theta^3 \qquad (1)$$

is used to represent the observations, the deviations of the different observations from this curve will be those shown in Fig. 1. The abscissæ are observed temperatures and the ordinates the deviations. This curve agrees to about 0°.001 with the data of

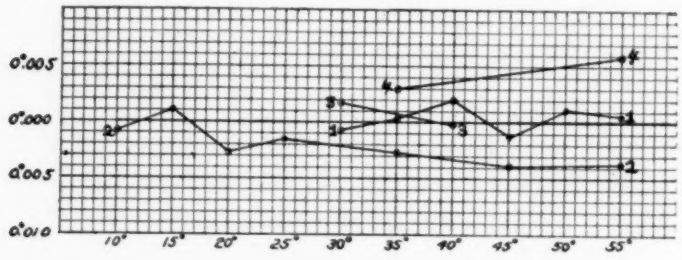

Fig. 1. Deviations of the observations of the first, second, third and fourth days.

the first day, but is about 0°.080 low at 100°, probably because the experimental data at 55° are especially low, a result of the leakage already mentioned. The curve

$$E = 155.311\theta + 0°.183\theta^2 - 0°.00014\theta^3 \qquad (2)$$

was passed exactly through 0°, 35°, 55°, 75° of the second set (Table I.). It agrees to 0°.002 or better at intermediate points and is thus quite as good as the data. At 100° it is probably 0°.006 low, though this error is no larger than the uncertainty of the observations at that point.

It thus appears that a cubic will express the electromotive force of these thermoelements from 0° to 100° with an accuracy nearly as great as can be expected in a comparison with the established temperature scale. The last result at 100° appears to show the effect of the negative cubic term, which has no physical significance, and increases disproportionately with increasing values of θ. Since we know no more of the actual physical function than that its curvature is somewhat less than that of a parabola, it would seem more logical and safe, in representing it, to stop short of a parabola in the first

place, instead of taking too great a curvature and then correcting it by the uncertain cubic term. With this idea in view, the subparabolic formula

$$E = 309.694\theta + 0.527080^{1.91} \quad (3)$$

was obtained for the same data as (2). It fits intermediate points even better than (2) but is 0°.028 higher at 100° (and therefore probably 0°.022 too high). That these two curves, after coinciding so closely up to 75°, should diverge so much in 25° more, is a striking illustration of the danger of extrapolating temperature curves. It also shows the possible value of the subparabolic formula, and this in spite of the fact that in this particular instance it is the cubic formula which agrees best with observation. But it is probable that the cubic expression is an exceptionally good fit for this particular function.

Methods of Calibration.—A thermoelement may be calibrated in three ways: (1) By comparison with a thermometer of another type. Here the thermoelement does not differ materially from any other thermometer which requires such calibration. (2) By direct comparison with a similar thermoelement. This can be done differentially, and may then be made probably the most accurate and almost the easiest of all thermometric operations. Even in the accessory apparatus, almost all errors disappear. (3) From fixed points alone. This method, while less convenient than either of the others, will, unless very good standards are available, usually be the most suitable. For the interval 0° to 100° the points 32°.384[1] (transition temperature of sodium sulphate), 58°.089[2] (transition temperature of manganous chloride) and the steam point seem very well adapted. Of these three points the calibration of a resistance thermometer would require only two.

The calibration of thermoelements might be greatly simplified if a stock of uniform calibrated wire should become available. It is possible that the calibration of the thermoelements made from such wire could then be determined with sufficient accuracy by using a single fixed point, for example, the steam point in addition to the reference point at 0°. Of course, a considerable amount of experi-

[1]Bull. Bureau of Standards, 3, 661, 1907.

[2]Richards and Wrede, Proc. Am. Acad., 43, 343, 1907.

ment would be necessary to determine what degree of accuracy could be secured by this method.

Summary.—A pair of copper-constantan thermoelements for use in calorimetric work was calibrated by comparison with resistance thermometers to an accuracy of 0°.004. It seems probable that the accuracy of the calibration could be considerably exceeded. A cubic equation probably represents the relation between temperature and electromotive force, in the interval 0° to 100°, with an accuracy of 0°.005 or better. New thermoelements may be very conveniently calibrated by direct differential comparison with those whose calibration is already known.

WASHINGTON, D. C.,
March 31, 1910.

TABLES OF DEMAGNETIZING FACTORS FOR IRON RODS.

By C. L. B. Shuddemagen.

When an iron rod is subjected to a magnetic field H_0 in a long solenoid it becomes magnetized, and its own magnetism gives rise to a magnetic field H_m which is everywhere superposed upon the original field H_0 due to a current in the solenoid itself, which latter is uniform within the solenoid, at least near the middle part of its length. The vector addition of these two fields gives the resultant magnetizing field H, which controls the actual intensity of magnetization I at every point of the iron rod. The following formulas now define the "susceptibility" k, the "magnetic induction" B, and the "permeability" μ:

$$I = kH,$$

$$B = 4\pi I + H = (4\pi k + 1)H = \mu H.$$

The field H_m is in all parts of the iron rod except near its ends, directed so as to weaken the field H_0 parallel to the axis of the rod. It is therefore usually spoken of as a "demagnetizing field," since when acting alone it always tends to demagnetize the rod. Near the middle of the iron rod H_m is directed oppositely to H_0 so that the resultant field there is

$$H = H_0 - H_m.$$

Now if the iron rod be magnetized continuously from neutrality to any state in which the intensity of magnetization in the middle part of the rod is I, then H_m will depend on I, and we can write

$$H_m = NI,$$

where N is some function of I to make the equation true. It was formerly thought that N was constant and depended only on the ratio of the length to the diameter of the cylindrical iron rod, or $m = L/D$. Investigations by Benedicks[1] and by the writer[2] showed,

[1]Wied. Ann., 6, 726–760, 1901.

[2]Proc. Amer. Acad., 43, 185–256, 1907.

however, that N is only approximately constant in the interval from $I = 100$ to $I = 800$. Beyond this it decreases rapidly to a minimum value as the magnetization approaches saturation. Moreover, the N varies also for different absolute values of D, the diameter of the iron rod, being somewhat less for thick rods than for the thin ones, when L/D remains constant.

In the experiments of the writer the iron rods magnetized varied from 0.3175 cm. to 1.905 cm. in diameter. Two magnetizing solenoids were used, for which

No. 1, length = 207.7 cm.; $H_0 = 20.5 \times$ (no. of amperes).
No. 2, length = 485.3 cm.; $H_0 = 27.064 \times$ (no. of amperes).

The magnetic induction in the middle part of the iron rod was found by wrapping a secondary coil around it, connecting it in series with a Thomson galvanometer and a known resistance, and observing the ballistic throw when the current, and the field H_0, were either suddenly increased (method of steps) or completely reversed (method of reversals). The galvanometer was calibrated ballistically by discharging a known quantity of electricity through it from a condenser.

Magnetization curves of B *vs.* H_0 were thus obtained for many iron rods. Long rods were used to get the first curves, and they were then progressively cut down in length in order to obtain rods for which m $(=L/D)$ was smaller. Thus for a constant diameter a series of magnetization curves for various m's were obtained. From these curves a close approximation to the "normal curve," or magnetization curve or an infinitely long rod, for which there would be no demagnetizing field, can be obtained. Having found this "normal curve" it is easy to find the demagnetizing field H_m $(=NI)$ for any value of the magnetic induction B observed in a rod with a given ratio m. It is simply the horizontal distance between the normal curve and the one for m, measured on a level with the B considered, in the scale-units used for H_0. This H_m is the amount by which the curve for m must be "back-sheared" to the left, in order to give a point on the normal magnetization curve, from which the true permeability of the iron must be calculated.

This demagnetizing field H_m may be expessed in two ways:

$$H = H_0 - H_m = H_0 - NI,$$

$$H = H_0 - KB;$$

and the latter is evidently the easier to use if one of the ballistic methods of measuring the magnetic induction B is used; while if I is measured by a magnetometric method, the first equation is preferable.

For convenience in correcting the original field H_0 because of the demagnetizing field H_m the writer has, from the results of his experiments, constructed the two tables of "demagnetizing factors," N and K, for various ratios of m, or L/D and, for various diameters, D, of cylindrical iron rods of the common Bessemer steel.

It will be noticed that the demagnetizing effect is somewhat greater in the case when the method of steps, or slow increase of magnetic field H_0, is used, than when H_0 is suddenly reversed. It seems as if the N and K were practically constants for any iron rod whose diameter is 0.6 cm. or over, provided L/D is the same. However, as the diameter of the rod is made smaller, keeping L/D constant, the demagnetizing effect seems to increase continuously.

Suppose n secondary turns are wound around the middle part of a cylindrical iron rod of length L cm. and diameter D cm. Let this rod be placed inside a still longer magnetizing solenoid, and parallel to its axis. The two ends of the secondary coil are to be twisted together and led out from one opening of the solenoid to the terminals of a ballistic galvanometer; usually various known extra resistances must also be included in this circuit in order to regulate the ballistic throw. Then the charge Q which passes through the galvanometer, resulting in a throw of t cm., when the total number of magnetic lines through the secondary coil is suddenly changed by ΔN, will be

$$Q = n \cdot \Delta N/R = kt,$$

where R is the total "apparent resistance "of the circuit, and k is the constant for ballistic throws. The change in the magnetic induction B will be

$$\Delta B = \frac{\Delta N}{A},$$

$$A = \pi(D/2)^2 = \text{cross-section of the rod.}$$

Values for N.

m	Method of Steps.		Method of Reversals.		
	D = 0.32 cm. (1/8 in.).	D = 0.6–2 cm. (1/4–3/4 in.).	D = 0.32 cm. (1/8 in.).	D = 0.4 cm. (5/32 in.).	D = 0.6–2 cm. (1/4–3/4 in.).
10	.220	.204	.215	.210	.200
15	.117	.106	.113	.1095	.104
20	.074	.0672	.0720	.0690	.0655
25	.0515	.0467	.0503	.0480	.0455
30	.0382	.0344	.0372	.0356	.0335
35	.0295	.0264	.0279	.0273	.0258
40	.0234	.0211	.0228	.0217	.0206
45	.0191	.0172	.0186	.0177	.0167
50	.0160	.0144	.0154	.01475	.0139
60	.0115	.0104	.0112	.0107	.0101
70	.0087	.00795	.0085	.00816	.0077
80	.0069	.00625	.0067	.00645	.0061
90	.0056	.00507	.0054	.00521	.00495
100	.0046	.00420	.00445	.00432	.00410
125	.0031	.00280	.00297	.00282	.00273
150	.00222	.00204	.00214	.00209	.00198
175	.00166	.00154	.00161	.00158	.00150
200	.00130	.00120	.00125	.00122	.00117

Values for K.

m^2	Method of Steps.		Method of Reversals.		
	D = 0.32 cm. (1/8 in.).	D = .6–2.0 cm. (1/4–3/4 in.).	D = 0.32 cm. (1/8 in.).	D = 0.4 cm. (5/32 in.).	D = 0.6–2.0 cm. (1/4–3/4 in.).
10	.0175	.0162	.0171	.0167	.0159
15	.0093	.0084	.0090	.0087	.0083
20	.0059	.00535	.0057	.0055	.0052
25	.0041	.00372	.0040	.00382	.00362
30	.00304	.00274	.00296	.00283	.00267
35	.00235	.00210	.00222	.00217	.00205
40	.00186	.00168	.00181	.00173	.00164
45	.00152	.00137	.00148	.00141	.00133
50	.00127	.00115	.00122	.00117	.00110
60	.00091	.00083	.00089	.00086	.00080
70	.00069	.00063	.00067	.00065	.000613
80	.00055	.00050	.00053	.00051	.000485
90	.000445	.000404	.00043	.000415	.000394
100	.000366	.000334	.000354	.000344	.000326
125	.000247	.000223	.000236	.000224	.000217
150	.000177	.000162	.000170	.000166	.000158
175	.000132	.000122	.000128	.000126	.000119
200	.000103	.000096	.000100	.000097	.000093

If a Thomson ballistic galvanometer is used, then the "apparent resistance" will be the actual ohmic resistance; but if the galvanometer is a D'Arsonval, then the "apparent resistance" is usually much more, because of the counter E.M.F. induced in the galvanometer coil when it is set moving in its strong magnetic field. In the first case, the Thomson galvanometer may be calibrated ballistically by sending a known charge Q_0 from a condenser over the galvanometer circuit. Then if t_0 is the throw observed, we have $Q_0 = kt_0$; and, finally, the change in B when the throw t cm. was obtained, will be

$$\Delta B = \frac{Rkt}{nA} = \frac{RQ_0t}{nAt_0}.$$

If R is expressed in ohms, and Q in microcoulombs, then the right-hand members of this equation must be multiplied by 100 in order that ΔB may be expressed in maxwells per sq. cm.

In case a D'Arsonval galvanometer is used, it becomes advisable to calibrate its throws by means of known changes of magnetic flux through a secondary coil, including also in the galvanometer circuit the various extra resistances which are used in the work. It is usually most convenient to find B by reversing the current in the solenoid, thus reversing the B and H_0, and then in the formula above $\Delta B = 2B$.

Having calculated a series of values of B and the corresponding values of H_0 from the equation $H_0 = GI$, where I = number of amperes of current flowing through the solenoid, and G = the "constant" of the solenoid, the true magnetizing field is found by multiplying the B by the value of K for the m, or L/D, of the rod and subtracting this from H_0, in accordance with the formula $H = H_0 - KB$.

If m for the test-iron rod has a value different from those given in the table, the K for it may be found fairly accurately by interpolation on the curve of Km^2 *vs.* m, constructed from the data in the tables.

THE RADIUS OF MOLECULAR ATTRACTION.

BY C. W. CHAMBERLAIN.

INTRODUCTION.

SEVERAL attempts have been made to determine the magnitude of the radius of action of molecular forces, which in the following discussion will be called R, from observations made upon the phenomena of capillarity and thin liquid films. Plateau[1] considered it would be impossible for a liquid film to exist if the thickness of any portion of it was less than $2R$. Quinke[2] held that the tension in a liquid film becomes smaller when fewer liquid particles affect both its surfaces than in a thick liquid layer, or when there are fewer particles within a distance R from the liquid surface. This would be the case when a liquid film becomes thinner than $2R$. In this case the greater tension in the thicker portions of the film would cause it to burst. The same opinion seems to be held by Johonott.[3] Considering the capillary layer as a gradual transition from the liquid phase to the vapor phase Bakker[4] reaches the conclusion that a liquid film must always consist of a layer of liquid, limited by two complete capillary layers, and that the layer of liquid must have a minimum thickness equal to the radius of molecular attraction. Since the thickness of the capillary layer and the sphere of action are of the same order of magnitude, one can take for the radius of molecular attraction approximately the third part of the minimum thickness of a liquid film.

Leidenfrost,[5] by measuring the greatest diameter to which a bubble could be inflated from a known quantity of soap solution, found the limiting thickness of a liquid film to be $1.772(10)^{-4}$ cm.

[1]Recherches expérimentales, etc., 5e sér., Mém. d. Brux., T. 33., p. 44, 1861.

[2]Pogg. Ann., Bd. 137, p. 403, 1869.

[3]Phil. Mag. (5), 47, p. 501, June, 1899.

[4]Phil. Mag. (6), 17, p. 337, March, 1909.

[5]Leindenfrost, de aquæ communis nonnullis quatitatibus tractatus. Duisburgi ad Rhenum, 1756, 8vo, pp. 63–118.

Plateau[1] found the thickness of a liquid film which reflected the pale yellow of the first order of Newton's rings to be $1.135(10)^{-6}$ cm. Drude,[2] by considering the effect of capillarity on the reflection and refraction of light, determined the limiting thickness of a liquid film to be $1.7(10)^{-6}$ cm. The black spot in liquid films was first observed by Newton. Its limiting thickness was measured by Reinold and Rucker[3] and found to be $1.2(10)^{-6}$ cm. Johonott,[4] in a most excellent series of experiments, determined the limiting thickness of a liquid film to be $.6(10)^{-6}$ cm. If one accepts Bakker's conclusion the radius of molecular attraction deduced from Johonott's results is $2(10)^{-7}$ cm. Lord Rayleigh[5] has shown that a film of olive oil $2(10)^{-7}$ cm. thick will stop the movements of camphor particles on a water surface.

The first attempt to directly determine the value of R was made by Quinke.[6] He covered a glass plate with a wedge-shaped layer of another substance. The thickness of the edge of this wedge-shaped layer was zero. On this unmoistened wedge-shaped layer he placed a liquid. The angle of contact varied with the thickness of the wedge and first became constant at a point where the thickness was greater than R. For smaller thicknesses the underlying glass plate attracted the liquid and modified the angle of contact. The thickness of the wedge-shaped layer at any point was estimated by comparing its color with that of Newton's rings formed by an air layer of known thickness. In this manner Quinke found the value of R to be greater than $5(10)^{-6}$.

At the time this direct determination of the value of R was obtained no film had been measured the thickness of which was less than $1(10)^{-5}$ cm., or twice Quinke's value for R. Johonott's determination of the limiting thickness of a liquid film, and the value of R deduced from it, makes it impossible to longer accept Quinke's direct determination.

The following investigation was undertaken to find, if possible,

[1]Statique des Liquides, Vol. I., p. 210.
[2]Wied. Ann., Vol. 43, 1891, pp. 126–176.
[3]Phil. Trans., 1881, p. 447; 1883, p. 645, and 1893 (A), p. 505.
[4]Phil. Mag. (5), 47, p. 522, June, 1899, and (6), 11, p. 749, June, 1906.
[5]Proc. Roy. Soc., 47, p. 364, 1889–90.
[6]Pogg. Ann., Bd. 137, pp. 402–414, 1869.

the cause of the discrepancy between the value of R directly determined and its value deduced from measurements made on liquid films.

Method of Measurement.

Formation of Wedges.—A wedge-shaped layer of silver was formed upon glass. A series of trials led to the conclusion that there was room for improvement in Quinke's method of forming these wedges. He immersed in a silver solution a glass plate on which lay a glass rod of about 12 cm. radius. The silver layer deposited was uniform except under the rod, where the thickness gradually fell away. As the silver deposit is first formed at a point where the solution is thinnest, and thereafter the rate of deposition at this point is increased if there is the slightest motion in the solution, any small irregularity in the glass rod produces in the surface of the wedge irregularities often many times greater than in the rod. Were it feasible to employ one wedge these irregularities would cause no great difficulty. However, as the line of contact of the liquid with the wedge can best be determined in the capillary space between two wedges it is essential that both wedges have the same thickness at corresponding points. It is thus necessary to form two wedges exactly alike and with perfectly plane surfaces. To accomplish this two wedges were formed at the same time in a capillary space the walls of which were perfectly regular. The arrangement is shown in Fig. 1, *a* and *b*.

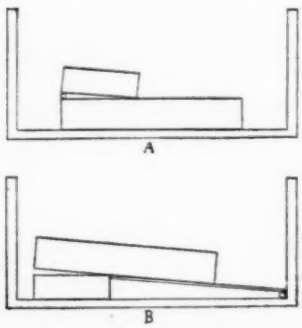

Fig. 1.

Neither of these methods was entirely successful, as it was found impossible to remove the silver deposited on the portion of the plate not enclosed in the capillary space without so weakening the edge of the silver wedge that it would be pulled off when the plate was immersed in water.

Fairly good wedges were formed by cathode evaporation. Fig. 2 shows the method of forming two wedges by shielding the two glass plates A and B by means of the glass plates D and E.

The most successful method of forming wedges is shown in Fig. 3.

A glass plate A with its lower surface optically plane was laid upon two plane-parallel plates B and C and separated from them at one edge by a small plate of glass .765 mm. thick. The plates A, B and C were all 6 × 8 cm. They were made by Petitdidier and were accurately plane to one twentieth of a light wave. The capillary

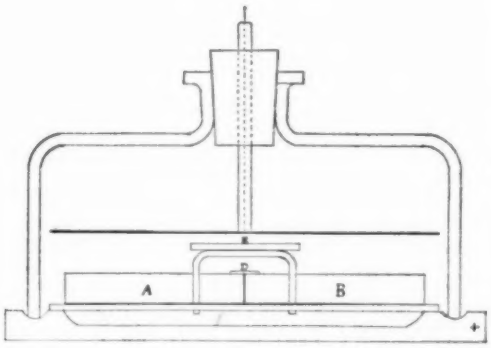

Fig. 2.

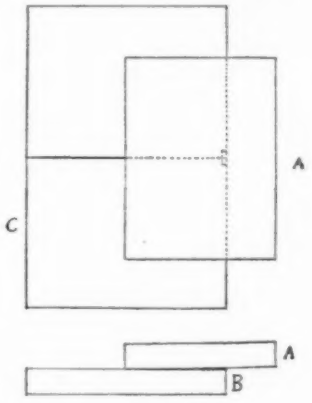

Fig. 3.

space between the plates was filled with Rochelle salt silvering solution by means of a small pipette. As all motion of the solution during the time of deposit was thus avoided good wedges with sharply defined edges were formed.

Of the large number of wedges produced twenty-three pairs were perfect enough to permit of measurement. These wedges were very transparent at their thickest points. Under a high-power microscope they appeared continuous, and adhered strongly to the glass if great care had previously been taken in the cleaning of the latter. In fact, it was not found possible to succeed with plates of optical glass which had been exposed for some time in the laboratory. The plates ultimately used were carefully sealed before shipment by the optician and were never laid away for any considerable length of time without having their surfaces protected by silver films.

Determination of Angle of Contact.—Two glass plates, with wedges formed in the manner shown in Fig. 3, were repeatedly washed with distilled water, dried, separated by three small pieces of glass .765 mm. thick, with the wedges facing each other, and bound together

by a rubber band. They were then placed in distilled water with the edges of the wedge-shaped silver films vertical. The water rose in the capillary space, forming at its upper surface a curve such as is shown in Fig. 4.

The average height y of the water at different distances x from a fixed reference point on the plates was measured by means of a

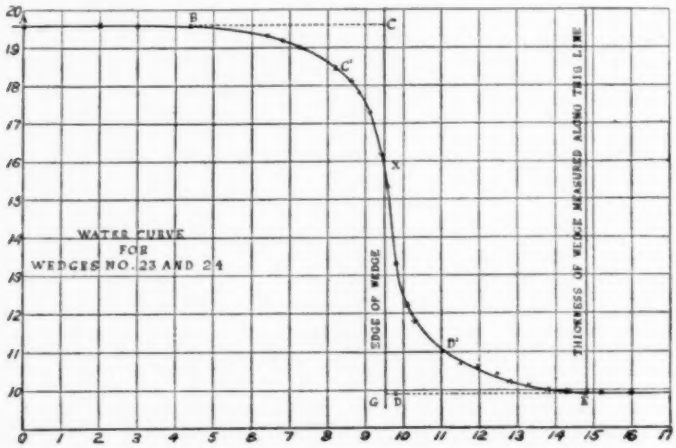

Fig. 4.

cathetometer whose telescope was provided with a filar micrometer eyepiece capable of horizontal motion. The results for wedges 23 and 24 are shown in Table I.

Quinke[1] and Laplace[2] have shown that

$$a^2 = H/\sigma,$$

(1) $$\cos w = y \cdot E/H$$

and

(2) $$\cos^2 w/2 = H'/H,$$

where a^2 is the specific cohesion of the liquid,

σ is the density of the liquid,

w is the angle of contact between the water and the plate,

y is the average height of the liquid,

E is the distance between the plates,

[1] Pogg. Ann., Bd. 135, p. 625, 1868, and Bd. 137, p. 406, 1869.

[2] Laplace, Méc. cèl., T. IV., p. 481.

H' is the attraction between the molecules of liquid and of the solid,

H is the attraction of the molecules of liquid for each other.

Accepting Quinke's value of a^2 for water as 15 the values for w and H'/H in the following table were computed by the aid of equations (1) and (2).

TABLE I.

x	D	y	w	H'/H
mm.	$(10)^{-6}$ cm.	mm.	° ′	
0	0	19.60	0	1
2	0	19.60	0	1
3	0	19.60	0	1
4.4	0	19.60	0	1
6.4	0	19.31	10	0.992
6.8	0	19.19	11 51	0.987
7.3	0	19.00	14 17	0.984
7.7	0	18.80	16 30	0.979
8.2	0	18.48	19 32	0.971
8.6	0	18.10	22 37	0.961
8.85	0	17.80	24 48	0.953
9.1	0	17.30	28 4	0.941
9.4	0	16.20	34 17	0.913
9.5[1]	0	15.85	36 4	0.904
9.6	0.05	15.30	38 43	0.890
9.8	0.15	13.20	47 17	0.839
10.1	0.31	12.20	51 31	0.811
10.3	0.41	11.80	53	0.801
10.55	0.53	11.50	54 6	0.791
11	0.76	11.00	55 34	0.783
11.5	1.02	10.70	56 56	0.773
11.95	1.25	10.60	57 16	0.770
12.45	1.60	10.40	57 58	0.765
12.8	1.68	10.20	58 39	0.760
13.3	1.94	10.10	58 58	0.758
13.8	2.19	10.00	59 20	0.755
14.3	2.44	9.95	59 31	0.754
14.8[2]	2.70	9.9	59 40	0.752
15.2	2.90	9.9	59 40	0.752
16	3.31	9.9	59 40	0.752

To determine the thickness of the silver wedge at the point where H'/H becomes constant the following procedure was adopted. A

[1]Edge of wedge.

[2]Thickness of wedge measured at this point.

small iodine crystal was placed on the wedge, changing it to silver iodide.

The chemical equivalent of silver, Ag = 107.9.

The chemical equivalent of silver iodide, IAg = 234.9.

The density of silver iodide, $d' = 5.602$.

The density of silver, $d^2 = 10.55$.

The index of refraction of silver iodide, $n' = 2.246$.

The relation between the thickness of the silver D and the thickness of the silver iodide E is as follows:

$$D = \frac{\text{Ag}}{\text{IAg}} \cdot \frac{d'}{d^2} \cdot E = .2439E.$$

In this manner the actual thickness of the wedge was increased approximately four times, and if one accepts Kundt's value for the index of refraction of silver the optical thickness is increased approximately twenty times. For the measurement of these thin films a new type of interferometer was devised.

THE COMPOUND INTERFEROMETER.

Light from a source S (Fig. 5) was divided into two portions by a thin silver film on the plane parallel plate C. The reflected portion was reflected by mirror A to mirror F, while the transmitted

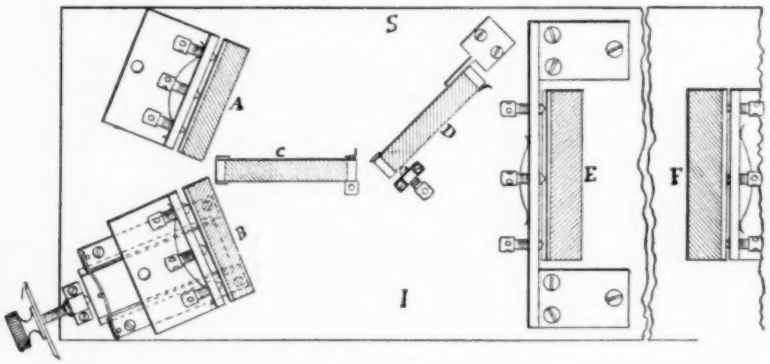

Fig. 5.

portion was reflected by the mirror B to the same mirror F. From the mirror F (Fig. 6) both rays, constantly parallel to each other, were reflected to the mirror E, back again to F, and so on, back and

forth between E and F any desired number of times, limited only by the angle of incidence on the mirror F, the angle between mirrors E and F, the vertical dimensions of E and F, and the intensity of the illumination. Having passed the two rays back and forth between E and F the desired number of times, they may be made to return on their paths, and partially reflected and transmitted at

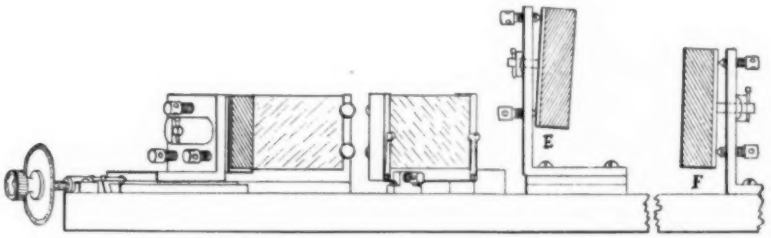

Fig. 6.

C be made to interfere when observed in the direction IC. The mirrors and plane parallel plates A, B, C and D were 2.5 × 4 cm. The mirrors E and F were 6 × 8 cm.

If the mirror F were divided vertically and one portion were moved parallel to the bed of the instrument the following relationship exists between the actual movement and the increase in the length of path of the corresponding beam of light.

$$D_n = 2d \cos nx \cos (n-1)x \left(\frac{1}{\cos nx \cos (n-1)x} + \frac{1}{\cos (n-1)x \cos (n-2)x} + \frac{1}{\cos (n-2)x \cos (n-3)x} + \cdots \frac{1}{\cos x} \right),$$

where x = angle between mirrors E and F,

D_n = actual distance passed over by the ray between the mirrors due to the movement of one portion of F,

n = the number of the order of the fringes, *i. e.*, n gives the number of times the ray is reflected by the mirror F,

d = actual movement of the mirror F parallel to the original path of the ray.

As the distance between the mirrors E and F was never less than 15 cm., it is readily seen that no appreciable error is introduced by assuming that the fringes of the second order are twice as sensitive

as those of the first order, those of the tenth order ten times as sensitive, etc.

The complete instrument is shown in Fig. 7. The wedge, the thickness of which was to be determined, was placed on the support shown midway between the two large mirrors. The instrument possesses many advantages for measurements of this character. The optical paths were parallel and near together. As the wedge must be formed on optical glass the measurement was greatly facilitated by employing for the compensating plate a portion of the same plate on which the wedge was formed. Interference fringes of various orders could be brought into the field of view by the adjustment of a single mirror. As regards convenience of use the instrument could be likened to a compound microscope with twenty objectives of varying focal length and all in the field of view at the same time.

Measurement of Wedges.—Having determined the point on a wedge at which H'/H became constant the thickness at this point was measured by means of the compound interferometer. A fiducial point for the instrument was obtained in the following manner. The glass plate with its wedge was fastened to the carriage of a dividing engine, and with one hundred strokes of a soft copper tool a furrow 2 mm. wide was planed in the silver at the desired point. The silver was then changed to silver iodide and the wedge placed in the path of one of the interfering beams of the interferometer. The retardation could be measured at the desired point by means of the distinct break in the straight line fringes as observed through the slit in the wedge.

The formula for obtaining the thickness of the silver from which the wedge of silver iodide was formed is

$$D = .2439 \frac{\delta\lambda}{N(n' - 1)}.$$

Where D = thickness of silver,

δ = observed displacement of the fringes,

λ = 589$\mu\mu$, the wave-length of light employed,

N = number of times light is passed through the silver,

n' = index of refraction of silver iodide.

Therefore $D = .1937/N$.

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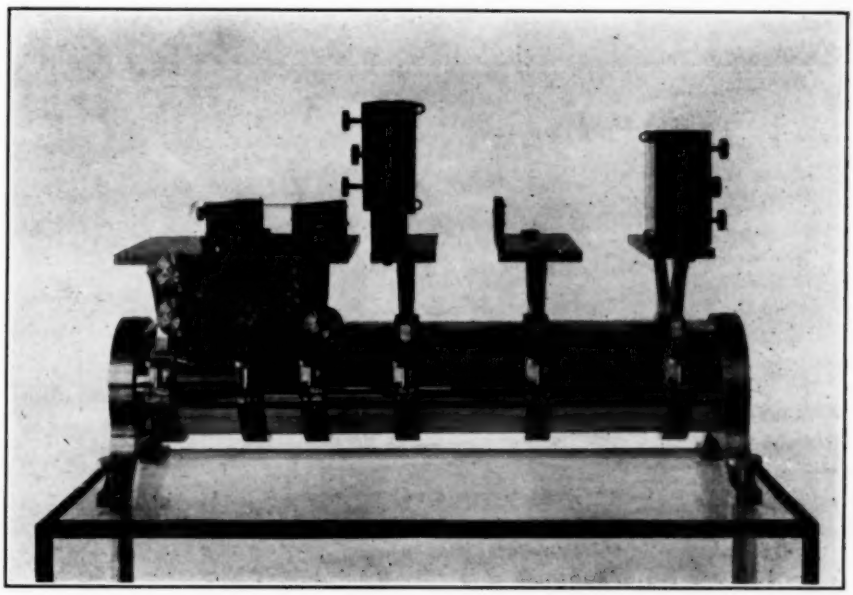

FIG. 7.

CHAMBERLAIN.

Radius of Molecular Attraction.

Table II. shows the results obtained for two pairs of wedges.

TABLE II.

Laboratory Number of Wedge	N	δ	D
10	2	.48	$2.7(10)^{-6}$
10	4	1.00	$2.8(10)^{-6}$
10	8	1.68	$2.6(10)^{-6}$
23	4	.96	$2.7(10)^{-6}$
23	8	1.98	$2.7(10)^{-6}$

As the interferometer clearly indicated the faces of the wedges to be accurately plane, it was possible to compute their thickness at any point having once determined the thickness for a given point. The thickness D of the silver in wedge 23 at varying distances from the edge of the wedge is recorded in the second column of Table I.

If Quinke's conclusion is correct we should take for R the value of D at the point where H'/H first becomes constant. We should thus obtain $2.7(10)^{-6}$ for the value of the radius of molecular attraction. This conclusion is incorrect, as the effect of surface tension in a direction parallel with the plates has been neglected. The effect of this neglected factor is to materially change the form of the curve of contact between the water and the plates. The effect of this neglected factor is not readily apparent in Quinke's experiment, since the wedges employed by him were double and practically covered the entire plate on which they were formed. In the improved form of wedge described above the effect of the neglected factor is readily seen. Referring to Table I. we observe that w and H'/H, both of which are computed from Quinke's formulas, decrease from the point $x = 4.4$, whereas they should remain constant to the point $x = 9.5$, since there is no silver on the glass up to this point. We thus see that w and H'/H cannot be computed from the formulas of Quinke and Laplace.

The above conclusion is shown graphically in Fig. 4, which represents the observed line of contact between the water and the plates for wedges 23 and 24. If we neglect the effect of surface tension in a direction parallel with the plates, the line of contact would pass through the points $ABCDEF$, C being at the edge of the wedge and

D at a point on the wedge where H'/H first becomes constant. Because of surface tension, however, the line of contact passes through the points $ABC'XD'EF$. The tension in the film decreases y in the region $BC'X$ and increases it in the region $XD'E$. D and not E is the point at which the thickness of the silver film is equal to R.

The point D is found in the following way. Call vertical distances above or below $ABCDEF \pm (v)$.

Let x = horizontal distance.

Let T = tension in surface film.

The equation for vertical equilibrium at each point $v \cdot x$ is

$$T \sin \theta = \int_x^E v dx.$$

Since the equation for vertical equilibrium is 0 at B and E

$$\int_B^E v dx = 0.$$

Therefore the observed curve $ABC'XD'EF$ bounds equal areas above and below the curve $ABCDEF$. By means of the planimeter and interpolation the correct position of the point D was found to be such that $GD/GE = 1/18$.

Since R = the thickness of the silver wedge at the point D, the radius of molecular attraction by direct measurement is found to be $1.5(10)^{-7}$.

THICKNESS OF THE BLACK SPOT IN LIQUID FILMS.

Johonott's excellent determination of the limiting thickness of liquid films would seem to leave little to be accomplished in that direction. He employed a Michelson interferometer and to obtain a deflection of 1.5 fringes was obliged to employ 215 films. As the second black film is of variable thickness his value of $6\mu\mu$ represents the mean thickness of a large number of second black films.

Since the compound interferometer is so readily adapted to the accurate measurement of a reasonably small number of films it seemed advisable to make a redetermination of the limiting thickness of liquid films.

As will be seen from Fig. 7 the optical parts of the instrument

are capable of rotation about a horizontal axis. In the figure the bed of the instrument is shown in horizontal position as used for

TABLE III.

Oleate of Soda.	Condition of Solution.	Age of Films.	Temperature of Films.	Number of Films.	Deflection of Fringe.	Thickness of Films.	Character of Films.	Calculated Thickness of Films.
%		h. min.				$\mu\mu$		$\mu\mu$
1–70	Partially sealed	9	22.2	53	2.6	10.8	$5B_2$	11.4
"	"	12	22.5	53	2.4	10.	$7B_2$	10.7
"	"	15	22.4	53	2.2	9.2	$10B_2$	10.1
"	"	1—40	21.8	51	2.4	10.3	B_1	10.3
"	"	1—55	22.3	51	2.4	10.3	B_1	10.3
"	"	10	19.2	45	1.6	8.8	$10B_1$	6.4
1–40	"	10	22.6	39	1.2	6.8	$3B_1$	6.3
"	Unsealed	15	22.6	24	.6	5.5	B_2	5.5
"	"	2— 5	27.2	41	1.2	6.5	"	6.5
"	"	2—13	27.2	36	1.0	6.1	"	6.1
"	"	2—18	27.2	33	.8	5.4	"	5.4
"	"	2—21	27.2	30	.8	5.9	"	5.9
"	"	10	27.6	49	1.4	6.3	"	6.3
"	"	20	27.7	42	1.0	5.3	"	5.3
"	"	18	24.6	40	1.2	6.6	"	6.6
"	"	22	24.9	34	1.0	6.5	"	6.5
"	"	27	25	32	1.0	6.9	"	6.9
"	"	10	26	49	1.4	6.3	"	6.3
"	"	17	26	48	1.4	6.5	"	6.5
"	"	12	26	46	1.4	6.7	"	6.7
"	"	16	26.6	45	1.4	6.9	"	6.9
"	Partially sealed	1	20.5	50	2.6	11.4	$4B_2$	11.9
"	"	1—15	20.3	50	2.6	11.4	$3B_2$	11.8
"	"	1—30	20.4	50	2.6	11.4	"	11.8
"	"	3—15	21.8	50	1.4	6.2	B_2	6.2
"	"	4—20	21.7	50	2.6	11.4	$3B_2$	11.8
"	"	4—25	21.7	50	2.4	10.6	$5B_2$	11.1
"	"	30	18.8	45	2.2	10.8	$7B_2$	11.7
"	"	25	19.4	39	1.0	5.6	B_2	5.6
"	Sealed	2—45	24.4	47	1.4	6.4	B_2	6.4
"	"	3—20	23.6	47	2.2	10.1	$4B_2$	10.8
"	"	4—45	23.5	46	2.2	10.5	$1B_2$	10.7
"	"	4—50	23.6	46	2.2	10.5	$1B_2$	10.7
"	"	24—05	26	31	.8	5.7	B_2	5.7

Mean thickness $B_1 = 11.1$.
" " $B_2 = 6.2$.

the measurement of the silver wedges. For the measurement of liquid films the bed of the instrument was rotated into a vertical position. Between the large end mirrors of the interferometer was placed a chamber closed at the ends with plane parallel optical plates. Within this chamber 53 films could be formed at one time in the path of one of the interfering beams of light. Both optical paths were thus in the atmosphere of the films, through which the light could be sent any number of times desired, by changing the angle between the end mirrors. As interference fringes of several orders were in the field of view at the same time, the varying thickness of the films could be followed from the time when they were first formed until they thinned to their limiting value.

Table III. shows the results obtained. Interference fringes of the fourth order were employed. The numbers given in the last column are calculated on the assumption that a first black film B_1 is twice the thickness of a second black film B_2.

SUMMARY.

Lord Rayleigh has shown that a film of oil $2(10)^{-7}$ cm. thick will stop the movement of camphor particles on a water surface.

Johonott's determination of the limiting thickness of liquid films is found to be correct. Measurements made upon a small number of films by means of a compound interferometer give the value $6(10)^{-7}$ cm. as the limiting thickness. Accepting Bakker's conclusion that R is approximately the third part of the minimum thickness of a liquid film the value of R determined in this manner is $2(10)^{-7}$ cm.

There is an error in Quinke's direct determination of R, due to a failure to consider all the effects of surface tension upon the free surface of a liquid included between two parallel glass plates, opposite portions of which are covered with wedge-shaped layers of silver. The correct value for the radius of molecular attraction determined directly is $1.5(10)^{-7}$ cm.

PHŒNIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
April, 1910.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

A NEW FORM OF ROTATING SECTORED DISK FOR SPECTRO-PHOTOMETRIC MEASUREMENTS.[1]

BY EDW. P. HYDE.

OF the various methods that have been used for varying the intensity of one source in spectro-photometric measurements, that employing a rotating sectored disk is perhaps the most accurate in general. To the author's knowledge two types of disks have been employed. First the elaborate disk of variable opening devised by Lummer & Brodhun, and second, the ingenious disk with rotating prisms designed by Brodhun. The former is expensive and complicated owing to the necessity of reading the divisions of a divided circle on a rapidly rotating disk. The latter, though simple, is not entirely satisfactory, owing to the glass parts which it contains and which, through possible selective absorption, render uncertain the readings in some cases. Moreover, the size of the opening as compared with the gross dimensions of the apparatus is such as to reduce considerably the available light.

Recently a new form of disk has been constructed and tested with great satisfaction. A disk of 10 cm. radius with a ball-bearing support is moved by a screw with a milled head along a wedge-shaped track normal to the axis of one collimator of the spectro-photometer. The track with its supporting frame-work is rigidly clamped to the support of the collimator. The disk which is driven by a separate motor with elastic belt is moved back and forth across the slit and quite close to it.

There are six openings in the disk, each of which is appoximately triangular with the apex at the periphery, and the base 4 or 5 cm. from the center. The angular opening varies, therefore, with the radial distance and so the percentage transmission can be measured by a divided circle on the screw moving the disk back and forth.

The edges or sides of each of the triangular openings instead of being straight lines, are arcs of a circle of a large radius. By these means it is possible to obtain a calibration curve such that a given angular turn of the screw produces very closely the same percentage change in transmission from

[1]Abstract of a paper presented at the Boston meeting of the Physical Society, December 28–30, 1909.

the maximum transmission near the center to 2 or 3 per cent. transmission near the periphery. At the point of maximum transmission the total angular opening is in the neighborhood of 320 degrees, thus reducing the quantity of light only about 10 per cent.

In conjunction with the description of this disk a method of correcting the observed energy curves for slit width is given briefly. This method was developed independently of that recently published by Nichols and Merritt and differs somewhat from it. It may, therefore, be of interest. It has been developed on the basis of the application of a substitution method of measurement, the comparison spectrum remaining constant both as regards distribution of energy and absolute intensity. Let $F_1(x)$ [where $\lambda=f(x)$] represent the luminosity curve of the impure spectrum of one source S_1; $R_1(x)$ the ratio of the luminosity curve of this source, to that, $F_0(x)$, of the comparison source S_0; and $R_2(x)$ the ratio of the luminosity of a second source, S_2, to that, $F_0(x)$, of the comparison source. If then, $f_1(x)$ and $f_2(x)$ represent the true distribution of energy for the two sources S_1 and S_2 to be compared, we have

$$\frac{f_2(x)}{f_1(x)} = \frac{F_1(x)\frac{R_2(x)}{R_1(x)} - K\Delta^2\left[F_1(x)\frac{R_2(x)}{R_1(x)}\right] + L\Delta^4\left[F_1(x)\frac{R_2(x)}{R_1(x)}\right], \text{ etc.}}{F_1(x) - K_1\Delta^2F_1(x) + L_1\Delta^4F_1(x), \text{ etc.}}$$

in which K, K_1, L, L_1, etc., are constants depending on the ocular slit-width d and the collimator slit-width a; and

$$\Delta^2 f(x) = \left[f\left(x+\frac{d+a}{2}\right) - f(x)\right] - \left[f(x) - f\left(x-\frac{d+a}{2}\right)\right],$$

$$\Delta^4 f(x) = \left[\Delta^2 f\left(x+\frac{d+a}{2}\right) - \Delta^2 f(x)\right] - \left[\Delta^2 f(x) - \Delta^2 f\left(x-\frac{d+a}{2}\right)\right].$$

As is evident from the equation it is necessary to know the actual luminosity curve $F_1(x)$ of the impure spectrum of one source. If the luminosity curve $F_0(x)$ of the comparison source is known, as stated previously the function $F_1(x)$ is readily determined.